A Review on New Technological Progress for Beneficiation of Refractory Phosphate Ore in China

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Abstract. The world is rich in phosphate resources, but the vast majority of the resources are of middle and low grade ores, and it is difficult to obtain high grade concentrate at a high recovery by using traditional separation methods. In this paper, the distribution and flotation processes of typical phosphate ores in China are introduced. Considering the current situation in phosphate ore beneficiation both home and abroad, the new trend of processing technology and reagents in China are summarized. Flotation is still regarded as the main processing method in phosphate ore beneficiation for a certain time in near future.

1. Introduction
According to the US Geological Survey (USGS) statistics, the world's phosphate reserves was 49.75 billion tons in 2015, and China has 13 billion tons. China's phosphate ore resources ranked the second in the world, but since 2006, many experts and scholars pointed out the current situation of phosphate ore resources, and issued an urgent appeal. In particular, the rational exploitation of China's phosphate ore resources and their sustainable utilization have been given a great deal of attention [1]. The next few years, China's major mining operation of the phosphate ore will focus on low-grade phosphate ore, which contains a large number of gangue minerals, such as silicon, magnesium and so on. Desiliconization of magnesium has been a problem of phosphate ore beneficiation. Mineral processors have been committed to the desilication and de-magnesium to improve the grade of the concentrate by applying new process and new reagents.

2. Phosphate ore resources and beneficiation process
China's phosphate ore resources are mainly distributed in Yunnan, Guizhou, Sichuan, Hubei and Hunan provinces, reserves account for about 74% of the national in total[2]. Although China is rich in reserves of phosphate ore, the phosphate ores are mainly of low-grade and lean type, which are difficult to process, and the easy-to-process ores are in quite a small number, and majorities are of poor availability [3] and refractory. In the past, the man beneficiation processes of phosphate ores were heavy medium separation technology, roasting digestion process and chemical beneficiation which are high in costs and low in efficiency.

2.1. Flotation process
2.1.1. Direct flotation process. Fang Shixiang[4] and other inventors disclosed the method of a low-grade mixed refractory colloidal phosphate in a positive way. The monomer of mixed type phosphate ore is firstly dissociated. After adding positive sodium carbonate, sodium silicate and other direct flotation regulators and fatty acid anion collectors, and then positive roughing flotation, positive cleaning floatation and positive scavenging floatation are applied tailings of the roughing flotaion and tailings of the cleaning floatation were combined to the positive scavenging floatation. When the mixed collophans is in the calcium-silica type, the concentrates of the positive scavenging floatation then returned to the positive roughing flotation, which forms a closed circuit operation; when the mixed collophan is of silica-calcium type, the concentrates obtained by scavenging floatation can be combined with the concentrates of cleaning floatation directly to the next reverse flotation operation. This invention simplifies the flotation process, is of simple operation, and greatly improve the recovery rate and the yield of concentrate, which is a kind of flotation method that is easy to operate, efficient to remove impurities and suitable to promote for the low-grade refractory mixed collophan.

2.1.2. Reverse flotation process. Liu Yuntao[5] invented a coarse-grain reverse flotation method for phosphate ore, which is characterized in that the low grade phosphate ore is crushed and grinded, and flotation feed size is of -0.074mm less than 50%, and then put it into the flotation tank with the pulp slurry concentration of more than 50%, pulp temperature between 10°C and 30°C, and then regulator--inorganic acid and mixed reverse flotation collector were added to, supplemented with water for reverse flotation operation, in which the tank product is low magnesium phosphate concentrate. The inventive method reduces the final concentrate magnesium content and improves the quality of the concentrate. The process has advantages of being simple in flow, good in separation performance and high in removal rate of magnesium.

Wang[6] and others improved the reverse flotation process of Yunnan Phosphating Group An increase of four sets of 120m³ flotation cell, which were arranged in parallel series for rougher flotation, making the roughing time increased from 14min to 17min. This makes the roughing process time much longer, reducing the pressure of the scavenging. Therefore, it stabilizes the system process, reducing the grade of P₂O₅ in the tailings and in the meanwhile, increasing the recovery.

2.1.3. Flocculation-flotation process. Wang Qiao[7] applied the flocculation to the sorting of phosphate ore. After series of experiments, the study shows that some flocculants involving Y3, F-08, N+09 and 850 can promote the flotation performance obviously. Of all the experimented flocculants, the flocculation F-08 has a great influence on the phosphate ore of Jinning, Yunnan Province. When the dosage of F-08 is 30g/t, the concentrate grade is 24.54% and the recovery is 85.30%, with beneficiation efficiency of 19.55%. Grade of the product increased by 4.17% than the grade of raw ore, and increased by 0.55% than that without adding flocculation. The recovery rate is 4.5% higher and the beneficiation efficiency is 3.95% higher than that without adding flocculation. The experiments results prove that this method is efficient in recovering the phosphate ore.

2.1.4. Direct-reverse flotation process. Fu Kewen[8] and others found that there are many problems using direct flotation to sort Dayukou open-pit mining of phosphate ore, as the concentrate foam is high in viscosity, the bubble is not easy to remove, and the concentrate is difficult to settle, the mass fraction of MgO in the concentrate is too high. Therefore, on the basis of laboratory tests, a new SP reagent was selected as an inhibitor of phosphate minerals, and a new technology of direct-reverse flotation was used to de-magnesium for the and rough concentrate. The results show that when the P₂O₅ of the raw ore is 17.90% and the MgO is 4.28%, concentrate of the P₂O₅ and MgO can be obtained at 31.62% and 0.74%, respectively, with the recovery of 81.35% MgO.
2.1.5. Reverse-direct flotation process. Huang Qi-mao[9] and others optimized the reagent system of the flotation according to ore properties of a low-grade silica-calcium phosphate ore in Hubei better selection indicators obtained by using reverse-direct flotation process are as follows: When the raw ore is of 17.09% P₂O₅ and the mass fraction of MgO is 5.29%, the obtained phosphate ore concentrate is 29.03% P₂O₅, with the recovery of 78.22%, and the mass fraction of MgO is 0.71%. This study provides a reference for the development and utilization of a low-grade silica-calcium collophanite.

2.1.6. Double-reverse flotation process. Li Songqing[10] and others studied the effect of the collector of BK425 for the double-reverse flotation, on a high-magnesium high-alumina phosphate ore in Guizhou. After two-staged grinding, the raw ore achieved the grinding fineness of -0.074 mm 75%. And phosphate concentrate assaying 33.97% P₂O₅, 0.73% MgO, with the recovery of P 73.71% was obtained by using closed-circuit process of the double-reverse flotation, and the sum of the sesquioxide (Al₂O₃ + Fe₂O₃) was 2.23%.

A medium-low grade collophane in Yunnan is a mixed type of phosphate ore, Wang Canxia[11] and others separated the phosphate ore minerals from the gangue minerals effectively by double-reverse flotation, which is based on the ore properties. When the grinding fineness is -0.074mm 88.36%, phosphate concentrate assaying 28.66% P₂O₅, 0.73% MgO, and 19.56% SiO₂, with the recovery of P 79.65% can be obtained.

2.2. Other methods
Ma Xiaoqing[12] invented a method that using medium mechanical processing to de-magnesium from the collophane ore. They added regulators and collectors of phosphate mineral flotation to the slurry of the broken silica-calcium phosphate ore then diluted with water, to conduct the flotation of phosphate mineral in the direct flotation system. After de-reagents and de-sliming, the concentrate enters the agitating tank to conduct the de-silication in the reverse flotation system to reversely float the silicious gangue minerals. The slurry of the rough concentrate of flotation after concentration enters the mechanical scrubbing system by adding a number of media to carry out series of scrubbing and desliming. The concentrate after filtration, and drying then becomes qualified phosphate concentrate for sale. This method proved to be more economical and practical by adopting. The method of mechanical de-magnesium which eliminates the need for grinding and reagents, simplifies the flotation process, reduces the cost and improves efficiency, and the obtained concentrate is low in MgO content and high in grade.

Li Ji[13] and others developed a method for the removal of silicic acid salts in low-grade phosphate ore. After magnetic separation, phosphate ore tailings were grinded to fineness of 90% -0.074mm and then some adjusters, collectors and silicic acid metal salt inhibitors were added into the pulp, by adopting the flotation flowsheet of one-stage roughing and two-stage cleaning, to achieve high-grade phosphate ore concentrate products. The invention realizes the efficient separation of telling the silicate metal salts apart from the associated low-grade phosphate ore, and the obtained phosphate ore ore containing over 34% P₂O₅, with the recovery more than 75%, less than 1.0% MgO, less than 2% Al₂O₃ + Fe₂O₃ content. The produced high-quality phosphate concentrate can be used as raw material for production of phosphate fertilizer, which proves that this method is a feasible mineral processing technology for utilization of a low-grade phosphate ore.

3. New reagents for the beneficiation of phosphate ores
The traditional flotation processes can be divided into 5 categories, they are: direct flotation, reverse flotation, direct-reverse flotation, reverse-direct flotation and double-reverse flotation. Generally, in the direct flotation, sodium carbonate is used as a regulator, sodium silicate as an inhibitor; in the reverse flotation, sulfuric acid as a regulator, phosphoric acid as an inhibitor[14]. Separation of
magnesium and silicon in phosphate ore has long been a difficult problem, and the traditional flotation method is not ideal enough to separate them.

3.1. Collectors
Zhang Ying[15], developed a new type of de-magnesium collector of FC-2B that can be applied to flotation of phosphate ore through series of separation tests on phosphate ore and dolomite, flotation test of the actual mineral results show that, FC-2B collector can effectively separate phosphate ore and dolomite. The raw ore assays 19.16% P Sub2O Sub5, 4.67% MgO, and the obtained concentrate assays 28.54% P Sub2O Sub5, with the recovery of 80.40%; 4.67% MgO, with the exclusion rate of 90.52%. And through infrared spectrum test, it is proved that the collector has a strong chemical adsorption on the surface of dolomite, and it keeps a better selectivity to dolomite.

Li Chengxiu[16] developed a new type of collector EM-LP-01 for direct flotation of collophane, with oleic acid, linoleic acid and linolenic acid-based (ratio of 3: 2: 1) mixed acid saponification and the SDS and OP-10 were mixed in 1: 1 to make the synergist. Then the mixed oil fatty acid soap and the combined synergist were mixed in 100: 20. This collector was applied to a silica-calcium collophane ore from Guizhou Wengfu Plant by adopting direct-reverse flotation process, under the condition of normal temperature After desilicication direct flotation of “one-stage roughing one-stage scavenging one-stage cleaning” and de-magnesium reverse flotation of “one-stage roughing one-stage scavenging”, concentrate assaying 30.86% P Sub2O Sub5 with the recovery of 89.57%, 0.77% MgO can be obtained. The new agent has a strong ability to selectively capture, and its solubility and dispersion are relatively good under the condition of room temperature.

3.2. Regulators

3.2.1 Modifying reagent. Ma Xianlin[17] invented a new regulator, using the mother liquor of production of sodium fluoride as pH adjustment reagent. The effects of mother liquor with different compositions on the residual MgO content in phosphate concentrate was studied. And the effects of H2SO4 and H2SiF6 in the mother liquor on the de-magnesium of phosphate ore were preliminary analysed. At the same time, the influence of the residual MgO content of phosphate concentrate that using the different proportions of mother liquor of villiaumite instead of sulphuric acid was studied. The results show that the fluoride mother liquor certainly has de-magnesium effect, and it can replace 50%~75% the consumption of sulphuric acid.

3.2.2 Depressant. Jiang Zhensheng etc. [18] invented a carbonate inhibitor. The inhibitor is an organic high molecular compound that contains a large amount of polar groups, such as carboxyl group, hydroxyl group, methoxy group, carbonyl group and amino group. The method has the advantages of simple process and no pollution. This inhibitor can effectively reduce the content of MgO in phosphate concentrate and COD in tailings. It also can reduce the dosage of regulator Na2CO3 in the process of direct phosphate flotation, which has good economic and environmental benefits.

3.2.3 Other regulators. Li Yaoji etc. [19] invented a method that using phosphoric acid residue as flotation regulator of phosphate ore. The residue of industry produced phosphoric acid is used as the raw material, through the pump the residue can be sent to the flotation regulator tank directly. After the flotation, phosphate flotation index can reach the requirements of dihydrate production of phosphoric acid. The invention has the advantages of simple process and applicability, and realizes the phosphate chemical mineralization coupling with phosphorite ore dressing, which has great significance in terms of resources and environment protection.

Zhao Jing, Chen Hongjian[20] found that in the mineral processing of phosphate ore (especially calcium or silica-calcium collophane, adding a small amount of TZ can significantly reduce the
viscosity of the flotation foam, improve the liquidity of the foam and significantly shorten the flotation time. Hence, the grade of phosphate concentrate can be significantly improved and it has a far-reaching impact on industrial production.

4. Conclusion
The phosphate ore reserves in China rank the second in the world, but the high-grade phosphate ore is deficient, which cannot meet the need of agriculture and other industries. The development and utilization of low-grade phosphate ores will last a long time for mineral processors to develop the new process with low cost and high efficiency. At present, the comprehensive utilization of phosphate ore resources in China has made certain achievements by mineral processors. Innovation on technological process for the refractory ore utilization should be conducted to produce the high grade phosphate concentrate of higher added value, and flotation will still be the leading technology for a long time. At the same time, developing more efficient flotation reagents and applying accurate and reasonable process to match with the ore properties become more and more important. Moreover, for the low grade and refractory phosphate ore beneficiation, more efforts should be paid on research of low cost and efficient beneficiation process.

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