Study of Reverse Flotation for a Collophanite with Sulfuric Acid

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Abstract: Mineralogy and flotation test of a collophanite were carried out. Under the grinding fineness of -0.074 mm 78%, the phosphorus concentrate contained yield of 53.83%, grade of 35.49%, recovery of 88.12%, MgO grade of 1.22% was obtained through a closed-circuit processes of one roughing, two cleaning and one scavenging with the sulfuric acid, TF-64. The quality of phosphorus concentrate had reached the II grade of HG/T2673-95 standard.

1. Preface
Phosphate rock is an important strategic resource and a non-renewable resource, which provides an important source of fertilizer for modern agriculture and is also the material basis of fine phosphorus chemical industry [1-3]. According to the composition of its impurity minerals, it can be divided into siliceous (mainly containing quartz, chalcedony, silicate, etc.), calcium-magnesium (mainly containing calcite and dolomite, etc.) and silicon-calcium-magnesium mixed phosphate ore [4-6]. The reserves of phosphate mineral resources of Sichuan province are large amount, but their phosphate mineral resources are mainly sedimentary phosphate rock deposits, which are very difficult to beneficiation and high cost of beneficiation. Enterprises have low economic benefits and some even deficiency [7-8].

In this paper, the mineralogy and beneficiation of a phosphate rock in China were carried out, and obtained better indexes.

2. Ore properties

2.1 Chemistry multiple analysis results of raw ore
Chemistry multiple analysis results of raw ore were shown in table 1.

| Items | P2O5 | MgO | CaO | Fe2O3 | Al2O3 | K2O |
|-------|------|-----|-----|------|-------|-----|
| Contents | 21.58 | 9.45 | 42.54 | 0.320 | 0.096 | 0.048 |
### Contents

- **0.150**
- **1.44**
- **17.75**
- **2.01**
- **4.616**
- **-**

#### 2.2 Composition of minerals

The ore is identified as phosphorus block rock ore through identification that the mineral composition is relatively simple. The main components in the ore are colloidal apatite, dolomite and a small amount of quartz (chalcedony). The dolomite phosphorite is mottled structure, dense striated structure and granular structure. The rock is a granular structure, which supported by matrix and basal cemented by basement.

#### 3. Experimental results and discussion

##### 3.1 Grinding fineness test

The grinding fineness test process and the agent conditions were shown in figure 1, and the test results were shown in table 2.

![Flowchart of grinding fineness test](image)

**Figure 1. Flowchart of grinding fineness test.**

**Table 2. Results of grinding fineness -0.074 mm test (%).**

| Grinding fineness | Items     | Yield  | Grade | Recovery |
|------------------|-----------|--------|-------|----------|
|                  |           |        | P_2O_5 | MgO      | P_2O_5 | MgO |
| 72.2             | Concentrate| 52.13 | 34.13 | 1.78     | 82.11  | 9.94 |
|                  | Tailings  | 47.87 | 8.10  | 17.57    | 17.89  | 90.06 |
|                  | Raw ore   | 100.00| 21.67 | 9.34     | 100.00 | 100.00|
| 78.6             | Concentrate| 49.34 | 35.70 | 1.14     | 81.24  | 6.01 |
|                  | Tailings  | 50.66 | 8.03  | 17.35    | 18.76  | 93.99 |
|                  | Raw ore   | 100.00| 21.68 | 9.35     | 100.00 | 100.00|
| 88.4             | Concentrate| 48.46 | 35.72 | 1.02     | 79.84  | 5.28 |
|                  | Tailings  | 51.54 | 8.48  | 17.18    | 20.16  | 94.72 |
|                  | Raw ore   | 100.00| 21.68 | 9.35     | 100.00 | 100.00|
It can be seen from table 2 that with the increase of grinding fineness (-0.074 mm), the yield of concentrate gradually decrease, the grade of \(P_2O_5\) increase, the grade of MgO decrease, and the recovery rate of \(P_2O_5\) decrease. When the grinding fineness -0.074 mm increase to 78.60%, \(P_2O_5\) grade in concentrate is 35.70%, MgO content is 1.14%, \(P_2O_5\) recovery rate is 81.24%, and MgO exclusion rate is 93.99%. The grade of \(P_2O_5\) in concentrate change little, and the recovery rate decrease slightly as the grinding fineness increase gradually. The grinding fineness of -0.074 mm was determined as 78.60% after comprehensive consideration.

3.2 Dosage test of sulfuric acid as roughing inhibitor

Figure 2 shows the test process of dosage test of sulfuric acid as roughing inhibitor. Grinding fineness was 78.60% of -0.074 mm and TF-64 dosage was 1.4 kg/t. The test results were shown in table 3.

It can be seen from table 3 that with the increase of the sulfuric acid dosage, the yield of concentrate gradually decrease, the grade of \(P_2O_5\) in concentrate gradually increase, the grade of MgO gradually decrease, and the recovery rate of \(P_2O_5\) gradually decrease, while the yield of tailings gradually increase, and the grade of \(P_2O_5\) in tailings decrease first and then increase. When the amounts of sulfuric acid exceeds 14 kg/t, the grade of \(P_2O_5\) in tailings increases slightly. Therefore, the dosage of sulfuric acid as roughing inhibitor was determined as 14 kg/t.

![Figure 2. Flowchart of roughing.](image)

| Sulfuric acid Dosage | Items   | Yield | Grade     | Recovery  |
|---------------------|---------|-------|-----------|-----------|
|                     |         |       | \(P_2O_5\) | MgO       | \(P_2O_5\) | MgO       |
| 12 kg/t             | Concentrate | 64.67 | 30.08     | 4.84      | 89.71      | 33.48     |
|                     | Tailings  | 35.33 | 6.31      | 17.60     | 10.29      | 66.52     |
|                     | Raw ore   | 100.00| 21.69     | 9.35      | 100.00     | 100.00    |
| 14 kg/t             | Concentrate | 60.79 | 31.67     | 3.94      | 88.76      | 25.65     |
|                     | Tailings  | 39.21 | 6.22      | 17.71     | 11.24      | 74.35     |
|                     | Raw ore   | 100.00| 21.69     | 9.34      | 100.00     | 100.00    |
| 16 kg/t             | Concentrate | 53.79 | 34.61     | 2.29      | 85.87      | 13.18     |
|                     | Tailings  | 46.21 | 6.63      | 17.57     | 14.13      | 86.82     |
|                     | Raw ore   | 100.00| 21.68     | 9.35      | 100.00     | 100.00    |

3.3 Dosage test of TF-64 as roughing collector

Figure 2 shows the test process of dosage test of TF-64 as roughing collector. Grinding fineness was 78.60% of -0.074 mm and sulfuric acid dosage was 14 kg/t. The test results were shown in table 4.
Table 4. Dosage results of TF-64 as roughing collector (%).

| TF-64 Dosage | Items      | Yield | Grade | Recovery |
|--------------|------------|-------|-------|----------|
|              |            |       | P₂O₅  | MgO      |
|              |            |       | MgO   | P₂O₅     |
| 1.0 kg/t     | Concentrate| 60.55 | 31.88 | 3.79     |
|              | Tailings   | 39.45 | 6.05  | 17.86    |
|              | Raw ore    | 100.00| 21.69 | 9.34     |
| 1.2 kg/t     | Concentrate| 57.46 | 32.78 | 2.98     |
|              | Tailings   | 42.54 | 6.69  | 17.37    |
|              | Raw ore    | 100.00| 21.69 | 9.35     |
| 1.4 kg/t     | Concentrate| 54.76 | 33.48 | 2.95     |
|              | Tailings   | 45.24 | 7.42  | 17.07    |
|              | Raw ore    | 100.00| 21.69 | 9.34     |

It can be seen from table 4 that with the increase of the TF-64 dosage, the yield of concentrate gradually decrease, the grade of P₂O₅ in concentrate gradually increase, the grade of MgO gradually decrease, and the recovery rate of P₂O₅ gradually decrease, while the MgO exclusion rate of tailings gradually increase. When the TF-64 dosage exceed 1.2 kg/t, the grade of P₂O₅ in tailing increase slightly, the grade of MgO change slightly, while the recovery of P₂O₅ decrease obviously. Therefore, the dosage of TF-64 as roughing collector was determined as 1.2 kg/t.

3.4 Dosage test of sulfuric acid in cleaning 1

Figure 3 showed the test process of sulfuric acid dosage test and conditions in cleaning 1. The TF-64 dosage was 0.6 kg/t. The test results were shown in table 5.

Table 5. Results of sulfuric acid dosage in cleaning 1 (%).

| Sulfuric acid dosage | Items    | Yield | Grade | Recovery |
|----------------------|----------|-------|-------|----------|
|                      |          |       | P₂O₅  | MgO      |
|                      |          |       | MgO   | P₂O₅     |
| 0.5 kg/t             | Concentrate| 48.86 | 35.42 | 1.33     |
|                      | Middlings| 8.74  | 15.65 | 11.33    |
|                      | Tailings | 42.40 | 7.07  | 18.21    |

Figure 3. Flowchart of sulfuric acid dosage test in cleaning 1.
It can be seen from table 5 that the grade of P$_2$O$_5$ in the middling is lower, the recovery rate is higher, indicated that it is necessary to add sulfuric acid in the cleaning 1. When the sulfuric acid dosage in cleaning 1 gradually increase, the concentrate yield, P$_2$O$_5$ and MgO grade change unsignificantly, while the exclusion rate of MgO gradually increase. The MgO exclusion rate has reached 63.10% with sulfuric acid dosage is 1.0 kg/t, while the MgO exclusion rate increase by only 0.90% with sulfuric acid increase to 1.5 kg/t. Therefore, the sulfuric acid dosage in cleaning 1 was determined as 1.0 kg/t.

3.5 Dosage test of TF-64 in cleaning 1

Figure 3 shows the test process of TF-64 dosage test and conditions in cleaning 1. The sulfuric acid dosage was 1.0 kg/t. The test results were shown in table 6.

| TF-64 Dosage | Items       | Yield | Grade | Recovery |
|--------------|-------------|-------|-------|----------|
|              |             |       | P$_2$O$_5$ | MgO | P$_2$O$_5$ | MgO |
| 0.4 kg/t     | Concentrate | 51.09 | 34.57 | 1.70 | 81.43 | 9.30 |
|              | Middlings   | 6.07  | 14.84 | 12.78 | 4.15 | 8.31 |
|              | Tailings    | 42.84 | 7.30  | 17.97 | 14.42 | 82.39 |
|              | Raw ore     | 100.00 | 21.69 | 9.34 | 100.00 | 100.00 |
| 0.6 kg/t     | Concentrate | 48.64 | 35.49 | 1.22 | 79.62 | 6.34 |
|              | Middlings   | 8.59  | 15.33 | 12.27 | 6.08 | 11.27 |
|              | Tailings    | 42.77 | 7.25  | 18.01 | 14.30 | 82.39 |
|              | Raw ore     | 100.00 | 21.68 | 9.35 | 100.00 | 100.00 |
| 0.8 kg/t     | Concentrate | 47.49 | 35.52 | 1.23 | 77.84 | 6.24 |
|              | Middlings   | 9.54  | 17.27 | 11.42 | 7.60 | 11.63 |
|              | Tailings    | 42.97 | 7.34  | 17.89 | 14.56 | 82.13 |
|              | Raw ore     | 100.00 | 21.67 | 9.36 | 100.00 | 100.00 |

It can be seen from table 6 that the recovery of P$_2$O$_5$ decrease gradually and the exclusion rate of MgO increase with the TF-64 dosage increase in cleaning 1. When the TF-64 dosage increase to 0.6 kg/t, the partly recovery of P$_2$O$_5$ is 92.91% and the exclusion rate of MgO is 64.00%. Therefore, the TF-64 dosage in cleaning 1 was determined as 0.6 kg/t.

3.6 Open-circuit test
After the above series of condition tests, the reagent system of roughing, scavenging and cleaning 1 were determined. The test process and operating conditions were shown in figure 4, and the test results were shown in table 7.

Table 7. Results of open-circuit (%).

| Items            | Yield | Grade | Recovery |
|------------------|-------|-------|----------|
|                  |       | P₂O₅ | MgO      |
| Concentrate      | 48.59 | 35.42 | 1.21     |
| Concentrate 1    | 4.31  | 32.78 | 2.35     |
| Tailings 1       | 4.96  | 10.93 | 12.10    |
| Tailings         | 42.14 | 5.96  | 19.13    |
| Concentrate +    | 52.90 | 35.21 | 1.30     |
| Concentrate 1    |       | 85.91 | 7.37     |
| Tailings 1 +     | 47.10 | 6.48  | 18.39    |
| Tailings         | 100.00| 21.68 | 9.35     |

Table 7 shows that the concentrate 1 with a grade of 32.78% is obtained after re-separation for middlings. The concentrate and concentrate 1 are combined as the final concentrate, which P₂O₅ grade is 35.21% and MgO grade is 1.30%, and P₂O₅ recovery rate is 85.91%.

### 3.7 Closed-circuit test

In order to ensure the concentrate quality of the closed-circuit test, we added a cleaning during the closed-circuit test. The reagents had been properly adjusted because there were some reagents brought back in the middlings. The closed-circuit test process and reagent conditions were shown in figure 5, the test results were shown in table 8.

Table 8 shows that the yield, P₂O₅ grade, MgO grade, P₂O₅ recovery rate of concentrate are 53.83%, 35.49%, 1.22% and 88.12%. The yield, P₂O₅ grade, MgO grade, P₂O₅ loss rate of tailings are 46.17%, 5.58%, 18.83%, 11.88% and 92.97%. Phosphorus concentrate quality had reached the II grade of HG/T2673-95 standard.
Figure 5. Flowchart of closed-circuit.

Table 8. Results of closed-circuit (%).

| Items           | Yield | Grade P2O5 | MgO | Recovery P2O5 | MgO |
|-----------------|-------|------------|-----|---------------|-----|
| Concentrate 1   | 13.46 | 35.48      | 1.22| 22.03         | 1.76|
| Concentrate 2   | 13.54 | 35.42      | 1.19| 22.12         | 1.73|
| Concentrate 3   | 13.43 | 35.61      | 1.25| 22.06         | 1.80|
| Concentrate 4   | 13.40 | 35.45      | 1.21| 21.91         | 1.74|
| Subtotal        | 53.83 | 35.49      | 1.22| 88.12         | 7.03|
| Tailings 1      | 11.54 | 5.58       | 18.83| 2.97         | 23.24|
| Tailings 2      | 11.48 | 5.46       | 18.95| 2.89         | 23.27|
| Tailings 3      | 11.60 | 5.64       | 18.79| 3.02         | 23.31|
| Tailings 4      | 11.55 | 5.63       | 18.74| 3.00         | 23.15|
| Subtotal        | 46.17 | 5.58       | 18.83| 11.88        | 92.97|
| Total           | 100.00| 21.68      | 9.35| 100.00        | 100.00|

4. Conclusions
(1) The phosphate ore has good washability, and the grinding fineness should be around -0.074mm of 78%.

(2) The phosphate concentrate with yield of 53.83%, P2O5 grade of 35.49%, P2O5 recovery of 88.12%, MgO grade of 1.22% was obtained by a closed-circuit processes of one roughing, two cleaning and one scavenging that used sulfuric acid and TF-64 as combination agents. The phosphorus concentrate quality had reached the II grade of HG/T2673-95 standard.

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