Process Simulation of the Influence of Phosphate Rock Impurities on the Production Index of Superphosphate

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Abstract. Through process simulation, the feasibility of the process and the influence of parameter changes on process indicators can be discussed, and guiding and optimizing the production process can be used. The impurities in phosphate rock mainly include components such as calcium carbonate, magnesium carbonate, iron trioxide, aluminum oxide and calcium fluoride, which presence can lead to changes in the production indicators of superphosphate. In this paper, the process simulation method is used to discuss the influence of the main impurity components in the phosphate rock on the production index of superphosphate. The results show that there is a linear relationship between the production index of superphosphate and the impurity coefficient. As the content of each impurity component increases, the effective P$_2$O$_5$ content and free acid P$_2$O$_5$ content of superphosphate products decrease, the free water content increases, the phosphate rock consumption quota decreases, and the sulfuric acid consumption quota increases. Among them, Al$_2$O$_3$ has the greatest impact on the product's effective P$_2$O$_5$ content and free water content, CaF$_2$ has the greatest impact on the product's free acid P$_2$O$_5$ content and phosphate rock consumption quota, and MgCO$_3$ has the greatest impact on the sulfuric acid consumption quota. The cumulative effect of various impurities on production indicators has a superimposing effect.

1. Introduction

Process simulation is a kind of virtual experiment which can avoid the limitation of raw materials and experimental conditions in conventional experiments, increase the selection and analysis range of variables, and carry out under multi factors and multi conditions [1]. The results of production process can be simulated by process calculation. Superphosphate (SSP) is a kind of phosphate fertilizer which can be produced with low and medium grade phosphate rock, and its price and fertilizer efficiency are welcomed by Chinese farmers [2-5]. Phosphate rock is the main raw material for the production of SSP, and its composition changes have a great impact on the production process indicators. The main component of phosphate rock is calcium fluorophosphate, which is usually accompanied by impurities such as carbonate and sesquioxide. Impurities in phosphate rock have a great influence on the production process. The types and contents of impurities are different, and their influence on the quality index and production consumption index of SSP products is also different.

Since phosphate rock usually contains multiple impurities at the same time, it is difficult to explore the influence of a certain impurity through physical experiments. Therefore, the influence of impurities in phosphate rock on production indexes can be discussed by using process simulation.
method, so as to timely control production parameters and ensure stable production when the composition of phosphate rock changes. In this paper, the production process of SSP is simulated by means of process simulation method, so as to explore the variation of main indexes of SSP with the content of impurities in phosphate rock.

2. The main impurity components in phosphate rock and their chemical reactions in the production of SSP

Generally, the composition of phosphate rock is expressed by the content of P$_2$O$_5$, CaO, MgO, CO$_2$, Fe$_2$O$_3$, Al$_2$O$_3$, F, acid insoluble A.I, etc., where P$_2$O$_5$ corresponds to the phosphorus content in the calcium fluorophosphate (Ca$_5$F(PO$_4$)$_3$) component, and CaO corresponds to the total calcium content in the Ca$_5$F(PO$_4$)$_3$, CaCO$_3$ and CaF$_2$ components, MgO corresponds to the magnesium content in the MgCO$_3$ component, CO$_2$ corresponds to the total CO$_2$ content in the CaCO$_3$ and MgCO$_3$ components, and F corresponds to the total fluorine content in Ca$_5$F(PO$_4$)$_3$ and CaF$_2$ components. In process calculation, it is necessary to convert the composition of phosphate rock into each component of phosphate rock, and then react with sulfuric acid or intermediate materials produced in the process to form different products. The composition of phosphate rock is different, and its influence on product quality and production consumption quota is also different.

In the production of SSP, the main chemical reactions are shown in formula (1) ~ (8) [5,6]. Among them, the main component Ca$_5$F(PO$_4$)$_3$ in phosphate rock reacts with sulfuric acid and intermediate phosphoric acid to form superphosphate products. The main components of the product are calcium dihydrogen phosphate monohydrate and calcium sulfate. Impurities react with sulfuric acid to form other components of SSP.

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\begin{align*}
7Ca_5F(PO_4)_3 + 35H_2SO_4 + 17.5H_2O &= 21H_3PO_4 + 35CaSO_4·0.5H_2O + 7HF \quad (1) \\
3Ca_5F(PO_4)_3 + 21H_3PO_4 + 15H_2O &= 15Ca(H_2PO_4)_2·H_2O + 3HF \quad (2) \\
(Ca,Mg)CO_3 + H_2SO_4 &= (Ca,Mg)SO_4 + H_2O + CO_2 \quad (3) \\
(Fe,Al)_2O_3 + H_2SO_4 + Ca(H_2PO_4)_2·H_2O &= 2(Fe,Al)PO_4 + CaSO_4 + 4H_2O \quad (4) \\
CaF_2 + H_2SO_4 &= CaSO_4 + 2HF \quad (5) \\
2CaSO_4·0.5H_2O &= 2CaSO_4 + H_2O \quad (6) \\
4HF + SiO_2 &= SiF_4 + 2H_2O \quad (7) \\
SiF_4 + 2HF &= H_2SiF_6 \quad (8)
\end{align*}
\]

3. Analysis and discussion of simulation results

The process simulation calculation method refers to the "dilute acid ore powder method calcium superphosphate production process calculation method" in the literature [5]. In order to study the influence of the impurity components in phosphate rock on the production process indexes, other parameters of the process should be fixed for comparison. Process calculation uniformly fixed raw material phosphate rock P$_2$O$_5$ content is 26%, phosphorus conversion rate is 96%; raw material sulfuric acid concentration is 68%, theoretical consumption; the F that escapes from the process is mainly SiF$_4$, and the evaporated water is 27% of the water brought in by phosphate rock and sulfuric acid [5]. The production index takes product effective P$_2$O$_5$ content, free acid P$_2$O$_5$ content and free water content as product quality evaluation indexes, and the consumption quota of phosphate rock and sulfuric acid (raw material consumption per unit of physical product) as process consumption evaluation indexes.

In order to explore the influence of the changes of various impurity components in phosphate rock on the production of SSP, Ca$_5$F(PO$_4$)$_3$ and acid insoluble matter A.I are used as the basic substances of phosphate rock. When investigating the influence of a certain impurity, the existence of other impurities are ignored. The amount of impurities is calculated according to the impurity coefficient (the mass ratio of impurities to P$_2$O$_5$) and the P$_2$O$_5$ content. Taking benchmark phosphate rock as raw material (that is, this phosphate rock only contains Ca$_5$F(PO$_4$)$_3$ and A.I components), the effective
$P_2O_5$ content of the SSP product obtained by simulation calculation is 16.00%, the free phosphoric acid $P_2O_5$ content is 1.55%, and the free water content is 8.60%, the phosphate rock consumption quota is 0.6410 t phosphate rock/t product, and the sulfuric acid consumption quota is 0.2683 t sulfuric acid/t product.

3.1. Influence of phosphate rock impurities on the effective $P_2O_5$ content of the product

Set the impurity coefficient of phosphate rock to vary between 0 and 0.1. Phosphate rock is composed of calcium fluorophosphate, acid insoluble matter and impurities. Except that the comprehensive term is composed of impurities with the same impurity coefficient, the others are single impurity terms. The simulation results of the effects of different impurities on the effective $P_2O_5$ content of SSP products are shown in Figure 1.

![Figure 1. Influence of phosphate rock impurities on the effective $P_2O_5$ content of the product.](image)

It can be seen from Figure 1 that as the impurity coefficient in the phosphate rock increases, the effective $P_2O_5$ content of the product decreases proportionally, among which the decrease range of $Al_2O_3$ and $Fe_2O_3$ is larger, and that of $CaCO_3$, $MgCO_3$ and $CaF_2$ is small. Since impurities will react with sulfuric acid, the amount of sulfuric acid will increase, and the amount of product obtained will increase accordingly, while the phosphorus content and conversion rate in the phosphate rock remain unchanged, so the effective $P_2O_5$ content of the product will decrease. It can be seen from the reaction formula (4) that during the production process, $Al_2O_3$ and $Fe_2O_3$ will consume the water-soluble phosphorus component of SSP (calcium dihydrogen phosphate monohydrate) to produce insoluble iron phosphate and aluminum phosphate, which ultimately leads to the effective $P_2O_5$ content of the product significantly reduce. When all impurities are present at the same time, the total sulfuric acid consumption of the phosphate rock increases, and the total amount of products also increases accordingly. Therefore, the comprehensive impurities lead to the largest decrease in the effective $P_2O_5$ content index.

Since each impurity has a linear relationship with the effective $P_2O_5$ content of the product, a straight line is fitted to each straight line to obtain the slope of each line (that is, the change rate of the effective $P_2O_5$ content of the product with the impurity coefficient) shown in Table 1. According to the data in Table 1, the cumulative value of the linear slope of each impurity is -51.6080, and the relative error between it and the linear slope of the comprehensive impurity is 7.13%. From this, it can be roughly judged that the effect of impurities is superimposed, which leads to a sharp decrease in the effective $P_2O_5$ content of the product.

| Impurity   | $CaCO_3$ | $MgCO_3$ | $Fe_2O_3$ | $Al_2O_3$ | $CaF_2$ | Comprehensive impurity |
|------------|----------|----------|-----------|-----------|---------|------------------------|
| Rate of change | -2.3037  | -2.7254  | -16.7920  | -26.0810  | -3.7019  | -48.1720               |
3.2. Influence of phosphate rock impurities on the content of free acid $P_2O_5$ of the product

The impurity coefficient of phosphate rock is set to vary between 0 and 0.1, and the process of producing SSP with different compositions of phosphate rock is simulated, and the influence law of impurities on the content of free acid $P_2O_5$ of the SSP product is obtained. The simulation results are shown in Figure 2.

![Figure 2: Influence of phosphate rock impurities on the content of free acid $P_2O_5$ of the product](image)

It can be seen from Figure 2 that with the increase of the impurity coefficient in the phosphate rock, the free acid $P_2O_5$ content of the product decreases proportionally, among which the decline of CaF$_2$ and Al$_2$O$_3$ is greater, the decline of Fe$_2$O$_3$ is the smallest, and the impact of comprehensive impurities is the largest. This is due to the different chemical reactions in the presence of various impurities, resulting in different reaction products and quantities, and the increase range of product quantity is different, which leads to the different decrease range of free acid $P_2O_5$ content in the products.

Table 2 shows the linear slope value (that is, the rate of change) between the free acid $P_2O_5$ content of SSP products and the impurity coefficient. It can be seen from Table 2 that the absolute value of the comprehensive impurity change rate is the largest, and its relative error with the cumulative value of the impurity change rate (-1.3803) is 7.10%. The influence of impurities on the content of free acid $P_2O_5$ of the SSP product has a superposition effect.

| Impurity     | CaCO$_3$ | MgCO$_3$ | Fe$_2$O$_3$ | Al$_2$O$_3$ | CaF$_2$ | Comprehensive impurity |
|--------------|----------|----------|-------------|-------------|---------|-----------------------|
| Rate of change | -0.2228  | -0.2636  | -0.2099     | -0.3259     | -0.3581 | -1.2888               |

3.3. Influence of phosphate rock impurities on the free water content of the product

Set the impurity coefficient of phosphate rock to vary from 0 to 0.1 to simulate the influence of different impurity phosphate rock on the free water content of SSP products. The simulation results are shown in Figure 3.
Figure 3. Influence of phosphate rock impurities on the free water content of the product.

It can be seen from Figure 3 that as the impurity coefficient in the phosphate rock increases, the free water content of the product increases proportionally, among which Al₂O₃ in the single impurity causes the largest increase in product free water, followed by Fe₂O₃, MgCO₃, CaF₂ and CaCO₃. This is because the chemical reaction of impurities of the same quality consumes different amounts of sulfuric acid, the amount of water brought in by sulfuric acid is different, and the amount of water produced by the reaction is also different (see reaction equations (3) ~ (7)). Therefore, the increase range of the product volume is different, and the water content in the product is different, so the free water content of the product increases differently.

Table 3 shows the rate of change of free water content of SSP products with impurity coefficient. It can be seen from Table 3 that the change rate of comprehensive impurities is the largest, and the relative error between it and the cumulative change rate of each impurity (48.6733) is 7.14%. The influence of impurities on the free water content of SSP products is superimposed.

Table 3. Variation rate of free water content with impurity coefficient in SSP products.

| Impurity   | CaCO₃ | MgCO₃ | Fe₂O₃ | Al₂O₃ | CaF₂ | Comprehensive impurity |
|------------|-------|-------|-------|-------|------|------------------------|
| Rate of change | 7.2482 | 8.5751 | 9.7178 | 15.0898 | 8.0424 | 45.4304 |

3.4. Influence of phosphate rock impurities on the consumption quota of phosphate rock

The impurity coefficient of phosphate rock is set to vary between 0 and 0.1 to simulate the influence of different impurity phosphate rock on the consumption quota of phosphate rock, which is the raw material for calcium superphosphate production. The simulation results are shown in Figure 4.

Figure 4. Influence of phosphate rock impurities on the consumption quota of phosphate rock.
It can be seen from Figure 4 that with the increase of the impurity coefficient in the phosphate rock, the consumption quota of the phosphate rock decreases proportionally, and the single impurity CaF$_2$ causes the largest decline in the consumption quota of the phosphate rock. The order of decrease is CaF$_2$>Al$_2$O$_3$>MgCO$_3$>Fe$_2$O$_3$>CaCO$_3$. This is because the phosphorus content of the phosphate rock remains unchanged during the process calculation. When impurities are present, the amount of sulfuric acid consumed by the chemical reaction increases, the product volume increases, and the amount of phosphate rock required to produce a unit product decreases, that is, the consumption quota of phosphate rock reduce.

Table 4 shows the change rate value of the consumption quota of SSP phosphate rock with the impurity coefficient. It can be seen from Table 4 that the absolute value of the comprehensive impurity change rate is the largest, and its relative error with the cumulative value of each impurity change rate (-0.5588) is 4.68%. The influence of impurities on the consumption quota of SSP production of phosphate rock is superimposed.

| Impurity | CaCO$_3$ | MgCO$_3$ | Fe$_2$O$_3$ | Al$_2$O$_3$ | CaF$_2$ | Comprehensive impurity |
|----------|----------|----------|-------------|------------|--------|------------------------|
| Rate of change | -0.0794 | -0.1092 | -0.0869 | -0.1350 | -0.1483 | -0.5338 |

3.5. Influence of phosphate rock impurities on sulfuric acid consumption quota

Set the impurity coefficient of phosphate rock to vary between 0 and 0.1 to simulate the influence of different impurity phosphate rock on the consumption quota of sulfuric acid as a raw material for calcium superphosphate production. The simulation results are shown in Figure 5.

It can be seen from Figure 5 that with the increase of the impurity coefficient in the phosphate rock, the sulfuric acid consumption quota increases proportionally. In a single impurity, MgCO$_3$ triggers the largest increase in the sulfuric acid consumption quota, and the order of increase in the rate of change is MgCO$_3$>CaF$_2$>CaCO$_3$>Al$_2$O$_3$>Fe$_2$O$_3$. This is because when the quality of each impurity is the same, the corresponding molar amount is different, so the amount of sulfuric acid consumed for chemical reaction is different, the product volume increase is different, and the amount of sulfuric acid required to produce a unit product is different, resulting in a different increase in sulfuric acid consumption quota.

Table 5 shows the rate of change of the consumption quota for sulfuric acid in SSP production with the impurity coefficient. It can be seen from Table 5 that the overall impurity change rate is the largest, and its relative error with the cumulative value of each impurity change rate (0.5743) is 7.13%. The influence of impurities on the consumption quota for sulfuric acid in SSP production is superimposed.
Table 5. Variation rate of the sulfuric acid consumption quota in SSP production with the impurity coefficient.

| Impurity          | Rate of change |
|-------------------|----------------|
| CaCO₃             | 0.1223         |
| MgCO₃             | 0.1447         |
| Fe₂O₃             | 0.0646         |
| Al₂O₃             | 0.1002         |
| CaF₂              | 0.1425         |
| Comprehensive impurity | 0.5361       |

4. Conclusion

Using the process simulation method, the influence of various impurities (CaCO₃, MgCO₃, Fe₂O₃, Al₂O₃, CaF₂ and comprehensive impurities) in the phosphate rock on the quality index and consumption index in SSP production was discussed. (1) The influence of phosphate rock impurities on the effective P₂O₅ content of SSP products is proportionally decreased, and the single impurity Al₂O₃ has the greatest impact; (2) The influence of phosphate rock impurities on the free acid P₂O₅ content of the product is proportionally decreased, and the single impurity CaF₂ has the greatest impact; (3) The influence of phosphate rock impurities on the free water content of the product is proportionally increased, and the single impurity Al₂O₃ has the greatest influence; (4) The influence of phosphate rock impurities on the consumption quota of phosphate rock is proportionally decreased, and single impurity CaF₂ has the greatest impact; (5) The impact of phosphate rock impurities on the consumption quota of sulfuric acid is proportionally increased, and the single impurity MgCO₃ has the largest impact; (6) When all impurities of phosphate rock exist simultaneously, it will affect the quality index and the influence of consumption quota is the largest, and the influence of impurities on each index has a superimposed effect.

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