

Migration and transformation behavior of harmful elements of lightweight ceramsite preparation from yellow phosphorus slag

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Abstract. In order to investigate the pollution behavior during the preparation of lightweight ceramsite from yellow phosphorus slag, the migration and transformation of the P-, S-, F-, and As-containing species in the heating system were simulated and calculated by FactSage 7.1 thermochemical software and databases. The results show that the P in the solid of $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$ is transformed to solid Fe_3P and a small amount of gaseous $(\text{P}_2\text{O}_3)_2$. The S-containing gaseous pollutants (CS_2 , S_2 , PS and COS) start to appear, while a large amount of S remains in the solid phase of CaS. A small amount of F is released in the form of SiF_4 , and all As exists in gaseous products. At temperatures ranging from 100-1100°C, P, S, F, and As elements cannot be transformed into the slag phase.

1. Introduction

Yellow phosphorus furnace slag is a by-product formed during the production of industrial yellow phosphorus by an electric furnace. For every 1 ton of yellow phosphorus that is produced, about 10 tons of slag are produced as a byproduct^[1]. When different cooling methods are used, the yellow phosphorus furnace slag can be divided into water-quenched slag and naturally-cooled slag. At present, there are many ways to utilize yellow phosphorus furnace slag resources, such as cement production^[2], subgrade materials^[3], agricultural silicon calcium fertilizer^[4], precipitated silica^[5], preparation of porous ceramics^[6], glass-ceramics^[7], and so on. Nowadays, the preparation of ceramsite from yellow phosphorus furnace slag^[8] has emerged as a new approach for its utilization. However, during the preparation process of ceramsites, harmful elements in phosphorus slag gradually release as the preparation temperature increases, which will pollute the surrounding environment and potentially be detrimental to human health. Therefore, it is necessary to predict the secondary pollutants that are released from yellow phosphorus slag when preparing ceramsite, and then effectively reduce and control it.



Factsage^[9] is a high temperature thermodynamic calculation program integrated with a thermochemical database, which is widely used in simulation calculation processes in the fields of environmental science, combustion science, material science, metallurgy, and others. For example, FactSage was utilized to simulate the phase transition process of glass-ceramics prepared from yellow phosphorus slag under calcination conditions^[10], as well as to predict the release of HCl gas during the combustion of straw when mixed with bituminous coal^[11].

This article is based on the analysis of the whole composition of yellow phosphorus water-quenched slag, and the preparation process of ceramsite from phosphorus slag mixed with clay in the literature^[12]. FactSage7.1 is used to simulate and predict the migration and transformation of sulfur, phosphorus, fluorine, and arsenic-containing products during the heating process. The aim of this paper is to provide a theoretical reference for controlling and reducing the secondary pollution produced during the preparation of light ceramsite from yellow phosphorus slag.

2. Experimental materials and methods

2.1 Materials

The yellow phosphorus slag derived from Jiangchuan, Yunnan (China) was crushed by a shredder and then dried at 100°C for 24h. After cooling, the phosphorous slag was sieved to 45 μm , and this material was used for further analysis.

2.2 Methods

The amounts of phosphorus, sulfur, fluorine, and arsenic in phosphorus slag were respectively determined by rapid phosphorus molybdenum blue colorimetric method, fluorine ion selective electrode method, sodium carbonate-zinc oxide semi melting gravimetric method, and atomic fluorescence spectrometry (AFS). The remaining components were determined by X ray fluorescence spectrometry (XRF). The conditions of XRF test were as follows: Rh target, voltage 50 kV, current 60 mA, qualitative analysis time was 0.2-0.8 s, quantitative analysis time was 20-40 s. The obtained compositions of the slag are shown in Table 1.

Table 1 compositions of yellow phosphorus slag (wt%)

| SiO ₂ | CaO | Al ₂ O ₃ | K ₂ O | Fe ₂ O ₃ | MgO | P | F | S | As |
|------------------|-------|--------------------------------|------------------|--------------------------------|------|------|------|-----------------------|-----------------------|
| 40.05 | 48.70 | 3.59 | 0.94 | 0.93 | 0.86 | 0.58 | 3.06 | 9.68×10^{-2} | 1.93×10^{-4} |

2.3 Raw material ratio and simulation calculation

Wu Yun^[12] et al. described the preparation process of lightweight ceramsite from yellow phosphorus slag. The raw material formula is shown in Table 2 and shows that the chemical composition of lightweight ceramsite is mainly SiO₂, CaO, and Al₂O₃. Therefore, the three components can be normalized, and the content of SiO₂, CaO, and Al₂O₃ after normalization are 51.35%, 37.04%, and 11.61%, respectively. In addition, Al₂O₃ (11.67g), SiO₂ (27.46g) and charcoal (6.12g) were added to the 100g phosphorous slag to obtain lightweight ceramsite of the SiO₂-CaO-Al₂O₃ system, and the formulation for this is shown in Table 3.

The composition and distribution of phosphorus, sulfur, fluorine, and arsenic in the heating process of lightweight ceramsite were calculated by using the module "Equilib" and databases "FactPs"^[9]. Before calculations, the calculation assumptions and parameters are as follows: (1) the gas phase equilibrium products after the reaction can be regarded as ideal gases, and if the high temperature molten phase occurs, it can be regarded as a real solution, (2) the input reactant is calculated according to the formula of lightweight ceramsite in Table 3, (3) the calculated temperature was maintained in the range of 100-1100°C, and the step length was 100°C, (4) the pressure was 101.325 kPa.

Table 2 Preparation of lightweight ceramsite from yellow phosphorus slag (wt%)

| Raw materials | CaO | SiO ₂ | Al ₂ O ₃ | MgO | Fe ₂ O ₃ | P ₂ O ₅ | F | C |
|-----------------------|-------|------------------|--------------------------------|------|--------------------------------|-------------------------------|------|-----|
| 66.7% Phosphorus slag | 43.36 | 37.49 | 3.52 | 1.73 | 1.67 | 3.41 | 1.06 | — |
| 28.6% Clay | 6.74 | 62.10 | 25.58 | 3.36 | 2.92 | — | — | — |
| 4.7% Charcoal | — | — | — | — | — | — | — | 100 |
| Total | 30.85 | 42.77 | 9.67 | 2.11 | 1.94 | 2.27 | 0.71 | 4.7 |

Table 3. The composition of the SiO₂-CaO-Al₂O₃ lightweight ceramsite (g)

| SiO ₂ | CaO | Al ₂ O ₃ | K ₂ O | Fe ₂ O ₃ | MgO | P | F | S | As | C |
|------------------|-------|--------------------------------|------------------|--------------------------------|------|------|------|-----------------------|-----------------------|------|
| 67.51 | 48.70 | 15.26 | 0.94 | 0.93 | 0.86 | 0.58 | 3.06 | 9.68×10 ⁻² | 1.93×10 ⁻⁴ | 6.12 |

3. Results and discussion

3.1 Prediction of gaseous pollution during firing

The existence of P, S, F, and As in each phase is shown in Figure 1 when the sinter mix reaches the sintering temperature of 1100°C and thermodynamic equilibrium is maintained. 96.2% of the phosphorus present in the sample exists in a stable solid phase, and the remaining phosphorus exists in the form of gaseous (P₂O₃)₂. The sulfur in the sample is a 95.15% solid phase pure species, and the remaining sulfur is in the form of CS₂, S₂, PS, and COS gases, respectively. Almost all of the fluorine elements exist in the form of solid CaF₂ and Ca₁₀(PO₄)₆F₂. All arsenic was transformed into a gaseous species such as AsS, As₄, As₃, As₂ and As. P, S, F and As can not be changed into the slag phase at 1100°C.

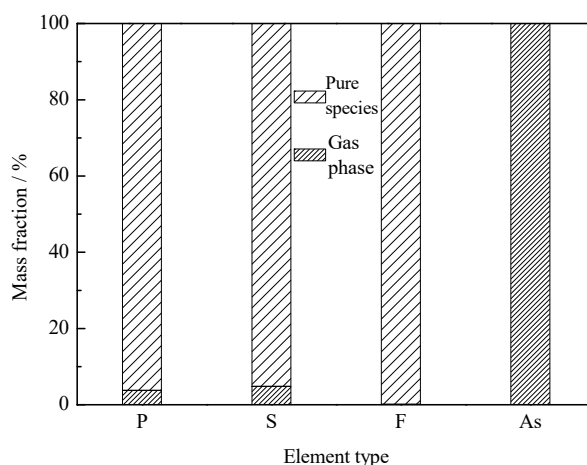
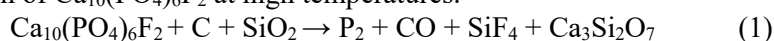


Fig.1 Distribution of phosphorus, sulfur, fluorine and arsenic in different phases at 1100°C

3.2 Migration and transformation of phosphorus

The distribution of the P-containing species in different phases during the heating process is shown in Figure 2. All phosphorus species exist in the form of solid-phase Ca₁₀(PO₄)₆F₂ at T < 900°C. Ca₁₀(PO₄)₆F₂ is relatively stable, and thermal decomposition is unlikely to occur at these temperatures^[13]. Therefore, the P-containing gaseous pollutants are not easily volatilized. When the temperature is higher than 1000°C, a small amount of Ca₁₀(PO₄)₆F₂ starts to transform into solid Fe₃P, and the content (15.38-31.1%) of Fe₃P gradually increases with increasing temperature because of the reaction of Ca₁₀(PO₄)₆F₂, C, and SiO₂^[14]. The P₂ produced from Reaction 1 then reacts with the Fe produced in Reaction 2 to produce Fe₃P, as shown in Reaction 3.^[14-15] When the temperature reaches 1100°C, a small amount of (P₂O₃)₂ gaseous pollutants begin to appear, which is due to the thermal decomposition of Ca₁₀(PO₄)₆F₂ at high temperatures.



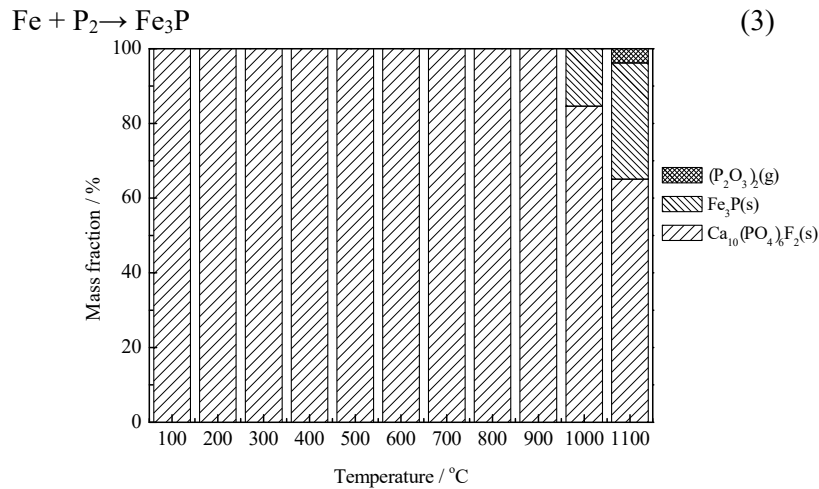


Fig.2 Distribution of the P-containing species in different phases during heating process

3.3 Migration and transformation of sulfur

Figure 3 illustrates the distribution of S-containing species in different phases during the heating process. In the temperature range of 100-300°C, sulfur is always present in the form of solid phase FeS_2 (99.91%) and As_2S_2 (0.09%). Then, as the temperature increases and remains in the range of 400°C to 1000°C, the solid phase As_2S_2 disappears, COS gas is produced and gradually increases with increasing temperature, but the increasing trend is not obvious. When the temperature reached 1100°C, all the solid phase FeS_2 decomposed. At this temperature, the sulfur products in the system were solid phase CaS (95.12%) and As_2S_2 (0.03%), and gas phase CS_2 (1.04%), S_2 (0.17%), PS (0.34%), COS (3.3%).

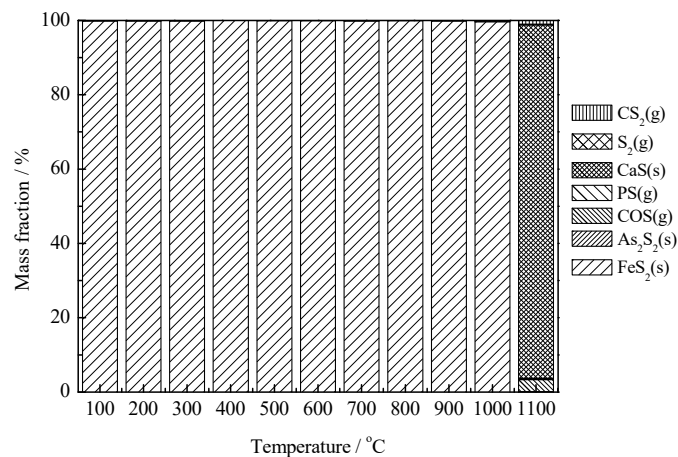


Fig.3 Distribution of the S-containing species in different phases during heating process

3.4 Migration and transformation of fluorine

The distribution of fluorine in each of the phases during the heating process is shown in Figure 4 and shows that fluorine is always present in the form of solid CaF_2 (96.12%) and $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$ (3.88%) in the temperature range of 100-900°C. When the temperature reaches 1000°C, the content of solid $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$ begins to gradually decrease, and the corresponding CaF_2 content gradually increases because of the solid phase reaction of $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$ at high temperatures (1000-1100°C), which is shown in reaction scheme No. (4)^[15]. At the same time, trace amounts of SiF_4 gas appear in the system, and the content of this gas gradually increases, which indicates that the high temperature solid state reaction between trace CaF_2 and SiO_2 in the mixture is the main cause of SiF_4 gas generation. This reaction is shown in reaction scheme No. (5)^[15].

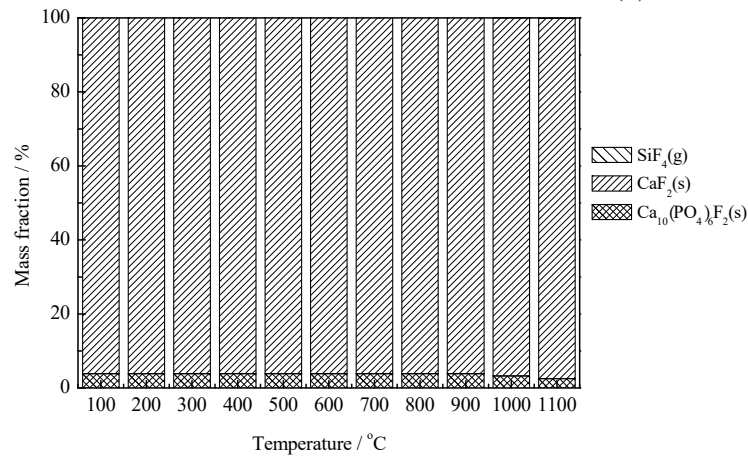
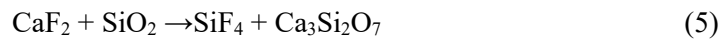
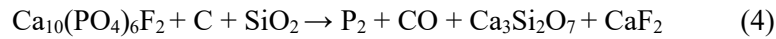


Fig.4 Distribution of the F-containing species in different phases during heating process

3.5 Migration and transformation of arsenic

The distribution of arsenic in each of the phases during the heating process is shown in Figure 5. Arsenic in phosphorous slag always exists in the form of As-containing gaseous pollutants in the entire temperature range of the experiment (100-1100°C), and below 400°C, all arsenic is present as As₄ gas. When the temperature rises to 500°C, gas phase As₂ begins to increase, and the content reaches a peak value at 1000°C, and above this temperature, the gas phase As₄ content begins to decrease. At 700°C, both gaseous phase products As₃ and AsS appeared in the system, and reached their peak values at 1000°C and 1100°C, respectively. At 900°C, gas phase As appeared, and the content (0.01-0.36%) increased with the temperature.

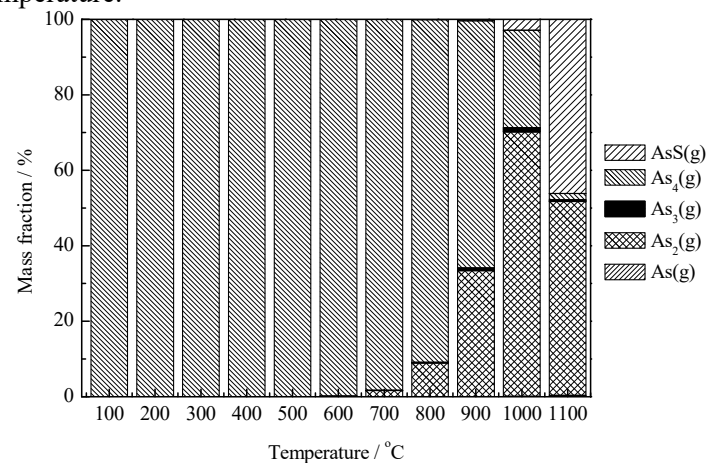


Fig.5 Distribution of the As-containing species in different phases during heating process

4. Conclusion

(1) When the calcination temperature reached 1100 °C, a small amount of phosphorus in the phosphorus slag formed (P₂O₃)₂ gas. Sulfur was mainly present in the form of solid CaS, and any residual sulfur formed S-containing gaseous mixture (CS₂, S₂, PS, and COS). The trace amounts of fluorine are released in the form of gaseous SiF₄. All arsenic is present in gaseous products.

(2) During the heating process, the phosphorus transforms from the solid phase Ca₁₀(PO₄)₆F₂ to the solid phase Fe₃P and gas phase (P₂O₃)₂. Sulfur exists in various forms, such as solid phase FeS₂, solid phase CaS, and S-containing gas phase products. Fluorine rarely enters the gas phase in the system, and it always exists in the form of solid phase CaF₂ and Ca₁₀(PO₄)₆F₂. All arsenic elements enter the

gas phase, and they are transformed from gas phase As₄ to an As-containing gas phase mixture.

Acknowledgments

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