Existing form and distribution of fluorine and phosphorus in phosphate rock acid-insoluble residue

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Abstract

The phosphorus-sulfur two-step production process was developed in the wet-process phosphoric acid industry to solve phosphogypsum pollution. However, phosphate rock acid-insoluble residue is produced during this process as a new type of solid waste, which had a high potential for recycling. For process reasons, this type of residue still contains a certain amount of fluorine and phosphorus, which has a massive impact on the potential uses of phosphate rock acid-insoluble residue. Therefore, X-ray photoelectron spectroscopy, Raman, electron probe spectroscopy, and scanning electron microscopy were used to examine the existing form and distribution of fluorine and phosphorus in phosphate rock acid-insoluble residue. The mass fraction of F and P₂O₅ were 9.407% and 11.862%, respectively. Fluorine existed mainly in the form of fluorite, fluorapatite and metal fluoride. Phosphorus existed mainly in the form of fluoroapatite, phosphate, hydrogen phosphate, and dihydrogen phosphate. The total phosphate, hydrogen phosphate and dihydrogen phosphate contents were much higher than that of fluoroapatite, whereas the fluoroapatite content was higher than that of fluoride and metal fluoride. Fluorine and phosphorus were distributed in the form of agglomerates in the phosphate rock acid-insoluble residue. Fluorine and phosphorus were partially correlated, showing a weak relationship in the high phosphorus area.

Keywords Acid-insoluble residue • Fluorine • Phosphorus • Existing form distribution

Introduction

In the wet-process phosphoric acid industry, the phosphorus-sulfur two-step method (As shown in Fig. 1) is a new technology for the clean processing of phosphate rock (PR). PR first undergoes acidolysis by phosphoric acid and is filtered to remove impurities. Sulfuric acid is then added to the filtrate for further extraction. The reaction rate of the process is gentle and controllable. The target product phosphoric acid has high purity, and the physical and chemical properties of phosphogypsum as a byproduct in the process can be improved significantly. Therefore, the rate of phosphogypsum utilization is improved dramatically to solve the environmental pollution problem of phosphogypsum (El Zrelli et al. 2018; Z.C.Kadirova et al. 2014; Shen et al. 2014). In the phosphorus-sulfur two-step process, there is a certain amount of insolubles solid material in the phosphoric acid acidolysis of PR, called phosphate rock acid-insoluble residue (PAIR). Its main component is siliceous rock, and a certain amount of metal compound, PAIR, has good application prospects. This is one of the key research issues of the phosphorus-sulfur two-step process. Combine PAIR is the characteristic of rich silicon. The application of PAIR in cooperating with other raw materials to prepare cement clinker and acting as a cement inert admixture is theoretically feasible. However, PAIR contains a certain amount of fluorine and phosphorus for technological
reasons, such as incomplete decomposition of PR and incomplete solid-liquid separation. Moreover, their existence and existence form have important impacts on the application strategy of PAIR. For example when preparing sulfoaluminate cement clinker, if the fluorine and phosphorus in the raw material components exist as organic fluorine and phosphorus pentoxide, the fluorine and phosphorus will volatilize before reaching the formation temperature of the clinker mineral phase and will not affect the clinker. However, clinker will be affected if the fluorine and phosphorus in the raw material components exist as CaF$_2$, phosphate and apatite. Related studies have shown that the presence of 0.6% CaF$_2$ in the raw material components can reduce the apparent activation energy of clinker and reduce the energy consumption of clinker sintering (Huang et al. 2014). A previous study examined the influence of fluorine and phosphorus on sulfoaluminate single mine, CaF$_2$ (0.5%) and Ca$_3$(PO$_4$)$_2$ (1%, calculated as P$_2$O$_5$) added to the raw materials, respectively. They found that F could promote the growth of sulfoaluminate crystals and expand the crystal size. [PO$_4$]$^{3-}$ can replace [SO$_4$]$^{2-}$ in the sulfoaluminate lattice, increase the content of sulfoaluminate cubic crystal form, reduce the content of the orthorhombic crystal form, and promote the formation of sulfoaluminate (Huang et al. 2016). In a study preparing sulfoaluminate cement with phosphogypsum, it was found that the F and P impurities in phosphogypsum can reduce the sintering temperature of clinker (Huang et al. 2019; Santoro et al. 1987), the cubic crystal form of the main mineral phase sulfoaluminate increases, and the orthorhombic crystal form decreases; the crystal form of dicalcium silicate also changed from the β type to the α' type (Huang et al. 2019). When researching dicalcium silicate single mine, [PO$_4$]$^{3-}$ can replace [SiO$_4$]$^{4-}$ into the dicalcium silicate crystal lattice, changing its crystal form. When [PO$_4$]$^{3-}$ exists in the form of Ca$_3$(PO$_4$)$_2$, it can help stabilize dicalcium silicate in the β, α' and α crystal forms (Benarchid et al. 2005; Saalfeld and Klaska, 1981). However, when it exists in the form of Ca$_3$(PO$_4$)$_3$OH, it can only help stabilize dicalcium silicate in the β and α' crystal forms (Benarchid et al. 2005). In the cement hydration stage, phosphorus will react with Ca$^{2+}$ and Al$^{3+}$ released by cement hydration to form insoluble phosphorus compounds to wrap the cement particles, which will hinder the progress of the cement hydration reaction and affect the development of cement compressive strength (Huang et al. 2019; Do Carmo Holanda et al. 2017). The degree of this adverse effect will vary according to the many forms of phosphorus. The negative effect of soluble phosphorus is greater, while the effect of insoluble phosphorus will be relatively small. Some studies examined the effects of different types of phosphorus on the hydration of cement. The degree of
negative influence was $H_3PO_4 > Ca(H_2PO_4)_2 \cdot H_2O > Ca_3(PO_4)_2 > CaHPO_4 \cdot 2H_2O$ (Huang et al. 2017). Among them, $CaHPO_4 \cdot 2H_2O$ can have a positive effect, which is conducive to the development of the compressive strength of cement. The effects of fluorine are similar to those of phosphorus. Soluble fluorine will react with $Ca^{2+}$ and $Al^{3+}$ to form insoluble fluorine to wrap around the hydration particles, hinder the hydration process, reduce the generation of hydration products, and affect cement performance (Guo et al. 2012). This insoluble fluorine is inert in water and will not affect the hydration reaction significantly.

PAIR has good potential utilization prospects, but research on fluorine and phosphorus in PAIR is still lacking. Therefore, in this paper, the PR in Guizhou, China, was used as the raw material to prepare PAIR using a phosphorus-sulfur two-step method. After analyzing the content, the existence form and distribution of fluorine and phosphorus in the PAIR using several characterization techniques, including X-ray fluorescence (XRF), X-ray diffraction (XRD), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), electron probe microanalysis (EPMA), scanning electron microscopy (SEM), and energy-disperse spectroscopy (EDS). The paper to provide a theoretical basis for the follow-up application of PAIR.

### Materials and methods

#### Materials

PR was purchased from Wengfu Group, with its main mineral composition and chemical composition shown in Fig. 2 and Table 1, respectively. Phosphoric acid (85% Industrial grade) was purchased from Sichuan Xiangruilong Instrument Reagent Co., Ltd.

#### Sample preparation and calculate

PR was pretreated by baking at 105 °C for 24 h and then milled into particles with a size of less than 200 mesh. The reaction of PR powder and 30% phosphoric acid ($P_2O_5$) was carried out with a mass ratio of 1:9 at 70 °C and a stirring speed of 300 rpm. After three hours, polyacrylamide with a concentration of 15 ppm was added as a flocculant with stirring for 2 min. Subsequently, the solution was filtered, washed with a bit hot water, and dried at 105 °C. The PAIR product was finally obtained after milling into particles with a size of less than 140 mesh.

The possible chemical reactions taking place during the acidolysis process of PR were calculated using HSC chemistry 9.3 software for thermodynamic calculation. The thermodynamic conditions for the spontaneous progress of each reaction were also determined, as listed in Table 2.

The element transfer factor (ETF) was estimated to determine the dynamic of the various elements from PR to PAIR. ETF was calculated using the following equation (Pérez-López et al. 2010).

$$ETF = \frac{m_{PAIR}}{m_{PR}} \times \frac{\text{Total element concentration}_{\text{PAIR}}}{\text{Total element concentration}_{\text{PR}}} \times 100\%$$

where $m_{PAIR}/m_{PR}$ is the mass ratio that was estimated to be 0.1. One hundred grams of PR will leave approximately 10g of PAIR due to acidolysis.

#### Characterization

Physical phase composition and chemical binding state of fluorine and phosphorus of PAIR was analyzed by using XRD, XRF, Raman and XPS.

XRD measurement was carried out with tube voltage of 40 kV, tube current of 30 mA, continuous scanning mode, scanning range 5–90°, scanning speed of 2°/min and step width of 0.2°. The data was analyzed by using MDI jade 9 software.

### Table 1 Chemical composition of PR determined by XRF (wt.%)

| Element | SiO$_2$ | CaO  | F    | P$_2$O$_5$ | Al$_2$O$_3$ | SO$_3$ | Fe$_2$O$_3$ | K$_2$O | Na$_2$O | TiO$_2$ | MgO  | Other |
|---------|--------|------|------|-----------|-------------|--------|-------------|--------|---------|---------|------|-------|
|         | 9.594  | 48.406 | 2.932 | 33.290    | 1.925       | 0.738  | 0.657       | 0.406  | 0.330   | 0.113   | 0.951 | 0.658 |
The conditions for XRF test included incident light energy of 16.4 keV, spot size of 100 μm × 100 μm, energy resolution less than 2 × 10^-4, information collection time of 3 min and parallel section polished line scan with 3 seconds for each point of information collection.

Raman test was performed under wavelength visible light at 532 nm, output power at 100 mW and scanning range of 100–3000 cm⁻¹. LabSpec6 and Knowitall software were applied to complete the processing and analysis of Raman data.

XPS test was performed by using a monochromatic Al Kα as the excitation source with the power of 200 W and the spot size of 500 μm. The binding energy was corrected by C(1s) peak at 284.8 eV of alkyl carbon or contaminated carbon. The basic vacuum during the analysis was set as 2 × 10⁻⁹ mbar. Avantage analysis software was used to complete the analysis and processing of the data.

The micro morphology of PAIR was analyzed by SEM and EDS equipment. The test conditions included acceleration voltage of 0.1–30 kV, electron beam current of 1 pA–2 nA,

### Table 2

| Equation | ΔG | Number |
| --- | --- | --- |
| Ca₅(PO₄)₃F + 7H₃PO₄ = 5Ca(H₂PO₄)₂ + HF(g) | ΔG = -0.389, ΔG < 0 | (1) |
| Ca₅(PO₄)₃F + 2H₂PO₄ = 5CaHPO₄ + HF(g) | ΔG = 13.443, ΔG > 0 | (2) |
| 3Ca₅(PO₄)₃F + H₂PO₄ = 5Ca₅(PO₄)₂ + 3HF(g) | ΔG = 79.165, ΔG > 0 | (3) |
| Ca₅(PO₄)₃F + 9HF(g) = 5CaF₂ + 3H₃PO₄ | ΔG = -54.193, ΔG < 0 | (4) |
| Ca₅(PO₄)₃OH + 7H₂PO₄ = 5Ca(H₂PO₄)₂ + H₂O | ΔG = -18.327, ΔG < 0 | (5) |
| Ca₅(PO₄)₃OH + 2H₂PO₄ = 5CaHPO₄ + H₂O | ΔG = -19.396, ΔG < 0 | (6) |
| 3Ca₅(PO₄)₃OH + H₃PO₄ = 5Ca₃(PO₄)₂ + 3H₂O | ΔG = -12.872, ΔG < 0 | (7) |
| Ca₅(PO₄)₃OH + 10HF(g) = 5CaF₂ + 3H₃PO₄ + H₂O | ΔG = 80.550, ΔG > 0 | (8) |
| 3CaMg(CO₃)₂ + 4H₃PO₄ = Ca₅(PO₄)₂ + Mg₃(PO₄)₂ + 6CO₂(g) + 6H₂O | ΔG = 70.811, ΔG < 0 | (9) |
| CaMg(CO₃)₂ + 4HF(g) = CaF₂ + MgF₂ + 2CO₂(g) + 2H₂O | ΔG = -56.877, ΔG < 0 | (10) |
| SiO₂ + 6HF = H₂SiF₆ + 2H₂O | ΔG = 32.912, ΔG > 0 | (11) |
| SiO₂ + 4HF(g) = SiF₄(g) + 2H₂O | ΔG = -18.146, ΔG > 0 | (12) |
| K₂O + H₂SiF₆ = K₂SiF₆ + H₂O | ΔG = 121.168, ΔG < 0 | (13) |
| K₂O + 2H₂PO₄ = 2KHPO₄ + H₂O | ΔG = 118.667, ΔG < 0 | (14) |
| K₂O + 2HF = 2KF + H₂O | ΔG = 102.531, ΔG > 0 | (15) |
| Al₂O₃ + 2H₂PO₄ = 2AlHPO₄ + H₂O | ΔG = -28.380, ΔG < 0 | (16) |
| Al₂O₃ + 6HF = 2AlF₃ + 3H₂O | ΔG = -73.037, ΔG < 0 | (17) |

### Table 3

| Elements | Oxide form | Single element form | PAIR | Oxide form | Single element form | ETF |
| --- | --- | --- | --- | --- | --- | --- |
| O | — | — | 44.724 | — | — | — |
| SiO₂ | Si | 52.708 | 24.313 | 54.938 | 3.563 | 23.138 |
| CaO | Ca | 15.211 | 10.637 | 3.142 | 3.142 | 3.142 |
| F | F | 9.472 | 9.407 | 32.305 | 32.305 | 32.305 |
| P₂O₅ | P | 11.862 | 5.083 | 3.563 | 3.563 | 3.563 |
| Al₂O₃ | Al | 4.454 | 2.331 | 3.563 | 3.563 | 3.563 |
| SO₃ | S | 3.050 | 1.198 | 41.328 | 41.328 | 41.328 |
| Fe₂O₃ | Fe | 1.387 | 0.946 | 21.111 | 21.111 | 21.111 |
| K₂O | K | 0.925 | 0.752 | 22.783 | 22.783 | 22.783 |
| Na₂O | Na | 0.085 | 0.063 | 2.576 | 2.576 | 2.576 |
| TiO₂ | Ti | 0.384 | 0.225 | 33.982 | 33.982 | 33.982 |
| MgO | Mg | 0.265 | 0.158 | 2.786 | 2.786 | 2.786 |
| Other | Other | 0.197 | 0.163 | 2.994 | 2.994 | 2.994 |
sample chamber vacuum of $10^{-4}$ pa, effective area of energy spectrum detector of 50 mm$^2$ and the energy resolution Mn K$_\alpha$ at 127 eV.

The element correlation and element distribution in PAIR were analyzed with an electron probe microanalyzer with the voltage of 20 kV, current of 20 nA and beam spot diameter of 5 μm.

### Results and discussion

#### Analysis of fluorine and phosphorus content in PAIR

Tables 3 and 4 list the XRF analysis results of PAIR. PAIR was mainly composed of O, Si, Ca, F, P, Al, S, Fe, K, Na, Ti and Mg, which were expressed as oxides with a total mass fractions of 99.803%. The sum of the mass fractions of SiO$_2$, CaO, F, P$_2$O$_5$, Al$_2$O$_3$, SO$_3$ and Fe$_2$O$_3$ was 98.144%. The mass fraction of SiO$_2$ was 52.708%, and the corresponding ETF value was 54.938%. This shows that PAIR is rich in silicon and only 54.938% of SiO$_2$ in PR remains in PAIR. This is similar to equations (11) and (12) that occurred during the acidolysis. The mass fraction of P$_2$O$_5$ was 11.862%, and the corresponding ETF value was 3.142%. This shows that 96.858% of P$_2$O$_5$ in PR entered the calcium dihydrogen phosphate solution, and only a tiny part remained in PAIR. The mass fraction of F was 9.407%, and the corresponding ETF value was 32.305%. This shows that most of the F in PR is volatilized in gaseous form; and only 32.305% F remains in PAIR in a reaction pathway similar to equations (4), (8), (10), (11), and (17). Only a small part of the original fluorine and phosphorus from PR remains in PAIR. However, the contents of P$_2$O$_5$ and F in PAIR were 11.862% and 9.407%, respectively. This is similar to the phosphorus and fluorine contents in many natural low-grade rocks (Mohammadkhani et al. 2011; Shariati et al. 2015). Therefore, PAIR still has industrial utilization value as inexpensive fluorine and phosphorus resources. In addition, as listed in Table 5, the trace elements in PAIR were Cl, Zn, Sr, Y, Zr, Ba, Cu, Cr and Rb. Among them, there were heavy metal elements, such as Zn, Cu, and Cr, which cause serious harm to the environment and human health. This shows that PAIR will inevitably pollute the environment if it is discarded in the environment without treatment. Therefore, the resource utilization of PAIR should not be delayed.

| Table 4 | Concentrations (% weight) of trace elements in PAIR determined by XRF |
|--------|------------------|
| Cl     | 0.015            |
| Zn     | 0.002            |
| Sr     | 0.045            |
| Y      | 0.003            |
| Zr     | 0.001            |
| Ba     | 0.061            |
| Cu     | 0.004            |
| Cr     | 0.006            |
| Rb     | 0.016            |

| Table 5 | Corresponding EDS results of the points displayed in Fig. 7 |
|---------|---------------------------------------------------------|
| Elements| O  | Si  | Ca  | F  | P  | Al | K  | Fe | (mol.%) |
| Point 1 | 28.51 | 1.90 | 18.94 | 46.09 | 4.56 | —  | —  | —  | —       |
| Point 2 | 36.80 | 4.01 | 17.81 | 4.82 | 4.36 | 2.20 | —  | —  | —       |
| Point 3 | 62.35 | 6.79 | 23.37 | —  | 4.96 | 2.53 | —  | —  | —       |
| Point 4 | 56.01 | 6.68 | 16.38 | 4.50 | —  | —  | —  | —  | —       |
| Point 5 | 65.61 | 6.82 | 19.89 | —  | 4.73 | 2.95 | —  | —  | —       |
| Point 6 | 52.26 | 9.77 | 8.90 | 20.09 | 5.43 | 2.86 | 0.71 | —  | —       |
| Point 7 | 52.30 | 13.55 | 6.91 | 14.00 | 6.63 | 4.89 | 1.17 | 0.50 | —       |
| Point 8 | 67.45 | 17.29 | 2.84 | 7.23 | —  | 4.04 | 1.15 | —  | —       |
| Point 9 | 40.03 | 59.97 | —  | —  | —  | —  | —  | —  | —       |

Fig. 3 XRD pattern of PAIR

Fig. 4 Raman spectra of PAIR
Existence form of fluorine and phosphorus in PAIR

XRD and Raman analysis

The XRF results indicated that the mass fraction of Na was below 0.065%. Therefore, the phases related to fluorine, phosphorus and sodium in PAIR can be ignored. Figures 3 and 4 display the XRD and Raman analysis results of PAIR. The crystal phase composition of PAIR was mainly quartz, apatite, pyrite, fluorite, and Ca(H₂PO₄)₂ (Fig. 3). Quartz, apatite, pyrite and fluorite are the residues from the acidolysis process, whereas the Ca(H₂PO₄)₂ is caused by the overproduction of Ca(H₂PO₄)₂ as the solution becomes saturated. As shown in Fig. 4, line (a) corresponded to the spectrum of phosphate (Montes-Hernandez and Renard, 2020; G. R. Sauer et al. 1994; Stammeier et al. 2018). The Raman shifts of four peaks were observed at approximately 459 cm⁻¹, 581 cm⁻¹, 952 cm⁻¹, and 1042 cm⁻¹, representing the symmetrical variable angle vibration peak, antisymmetric variable angle vibration peak, symmetrical stretching vibration peak, and antisymmetrical stretching vibration peak of PO₄³⁻, respectively. Line (b) corresponds to hydrogen phosphate (Xu et al. 1999). The Raman shifts of four peaks were observed at approximately 459 cm⁻¹, 581 cm⁻¹, 952 cm⁻¹, and 1042 cm⁻¹, representing the symmetrical variable angle vibration peak, antisymmetric variable angle vibration peak, symmetrical stretching vibration peak, and antisymmetrical stretching vibration peak of PO₄³⁻, respectively. Line (b) corresponds to hydrogen phosphate (Xu et al. 1999). The Raman shifts of five peaks were observed at approximately 459 cm⁻¹, 457 cm⁻¹, 590 cm⁻¹, 771 cm⁻¹, and 1034 cm⁻¹ were assigned to the PO bending (z') vibration, PO bending (z') vibration, PO bending (z') vibration, PO bending (z') vibration, PO bending (z') vibration, and PO stretching vibration, respectively.

XPS analysis

Figure 5 presents the high-resolution XPS spectra of F(1s) and P(2p). As shown in Fig. 5 (a), the F1s peaks of PR (683–687eV) and PAIR (682–690eV) showed large deviations because many new solid-phase fluorine substances are produced during the acidolysis of PR and remain in PAIR. Huge differences in the bonding type and the type of connecting atom were observed between the fluorine atoms of PAIR and the fluorine atoms of PR. The F1s spectra of PAIR were fitted (Gaussian-Lorentzian mixed peak shape function) to seven peaks to evaluate the fluorine substances of PAIR, as shown in Fig. 5 (b). According to the NIST (National Institute of Standards and Technology) database (Rumble Jr et al. 1992), the binding energy of F1s in the range, 682–686eV, is the same as that for the ionic bonding of metal fluoride. Therefore, by combining equations (4), (8), (10) and (16) and the known characterization results, the peak at 682.79eV is caused by the existence of KF (Murch and Thorn, 1980). The two peaks with a binding energy of approximately 684.59eV are caused by fluorite and fluorapatite residues (Murch and Thorn, 1980; Landis and Martin, 1984). Peaks 3 and 4 near 684.98eV and 685.70eV were assigned to the presence of CaF₂ and MgF₂ (Nefedov et al. 1977; De et al. 2016). The peak for F1s in the range of 686–688eV indicated a semi-ionic bond and covalent bond. Therefore, in combination with equation (13), it is believed that peak 5 at 686.63 eV was caused by the presence of K₂SiF₆ (Jorda et al. 1998). Peak...
6 at 687.80eV was assigned to AlF₃ (Kemnitz et al. 1996). Al is a special kind of metal, where only strong oxidizing elements can form ionic compounds with it (electronegativity differences between the two elements ≥1.7 and <1.7 results in an ionic bond and covalent bond). Although 687.80eV is in the range of 686–688eV, the difference in electronegativity between Al and F is >1.7, so the Al-F bond is still ionic. Other aluminum trihalide substances are covalent compounds. In the NIST standard database, when the binding energy of F1s exceeds 688.00eV, the corresponding substance is organic. In the F1s pattern, a weak peak (peak 8) could be separated at the binding energy above 688.00eV, indicating a trace amount of organic fluorine in the PAIR.

The P2p peaks of PR (131.5–136eV) and PAIR (132–136eV) were deviations (Fig. 5(c)). On the other hand, the degree of deviation was much weaker than that of the F1s peak. This is because the chemical binding state of the phosphorus atom from PR to PAIR has changed, but the change is not very large, and it exists in the form of a compound containing [PO₄] groups. As shown in (d) of Fig. 5, the P2p spectra of PAIR were fitted (Gaussian-Lorentzian mixed peak shape function) to four peaks to evaluate the phosphorus...
substances of PAIR. Combining equations (1), (2), (6), (7), (14), and (16) and known characterization results. Peak 1 with binding energy around 133.28 eV was caused by the presence of PO$_4^{3-}$ (Hanawa and Ota, 1992). Therefore, peaks 3 and 4 at 134.39 eV and 135.13 eV were assigned to HPO$_4^{2-}$ and H$_2$PO$_4^-$, respectively. Because every introduction of one hydrogen in PO$_4^{3-}$ will cause the corresponding peak binding energy to shift by approximately 1 eV (Hanawa and Ota, 1992). Peak 2 at 133.68eV was attributed to residual fluoroapatite (Landis and Martin, 1984).

**EPMA quantitative analysis**

According to the quantitative surface scan, correlation scatter plots of the element content of PAIR were obtained, as shown in Fig. 6. The correlation scatter plots included Ca-F, Si-F, Al-F, K-F, Fe-F, Ca-P, Si-P, Al-P, K-P, Fe-P, and Al-K. The Ca content showed a positive correlation with F and P. When the Si, Al, and K contents were extremely low, the contents of Si, Al and K were positively correlated with F and P. In other content ranges, these three elements were negatively correlated with F and P. The Fe content was negatively correlated with F and P over the entire range. A positive correlation was observed between the K and Al contents along the purple line, and no correlation was noted along the red line. A large number of points in the scatter chart followed the trend of the purple line, while only a small number of points followed the trend of the red line. These results indicated that a large amount of F and P were combined with Ca in PAIR. Only a small amount of F and P were combined with Si, Al and K. In particular, F and P in PAIR exist mainly as fluorite, fluorapatite, CaF$_2$, Ca(H$_2$PO$_4$)$_2$, CaHPO$_4$, and Ca$_3$(PO$_4$)$_2$. In contrast, only small amounts of F and P were present as AlPO$_4$, K$_2$PO$_4$, Mg$_3$(PO$_4$)$_2$, AlF$_3$, KF, MgF$_2$, K$_2$SiF$_6$, and organic fluorine. A weak positive correlation between P and Si was attributed to the existence of a solid phosphate solution similar to Al$_{0.33}$Si$_{0.48}$P$_{0.16}$O$_{2.2}$ (Xu et al. 2019). Some scholars have reported that Al$^{3+}$ + P$^{5+}$ can replace 2Si$^{4+}$ in a solid solution (Pownceby et al. 2019). Therefore, it is believed that this solid solution phenomenon occurred with a small amount of Si$^{4+}$ produced in equations (11) and (12) during the process of PR being acidified by phosphoric acid to form phosphate. The scatter plot of the S-Fe correlation indicated that the Fe and S contents were strongly positively correlated. Therefore, all the Fe in PAIR existed in the form of sulfide compounds (pyrite: FeS$_2$) and had no combination with F and P.
As shown in the O-F and O-P correlation scatter plot, the contents of O and F were positively correlated with the O content in the range of 0–3 wt. %, due mainly to the presence of fluorapatite. The contents of O and P were positively correlated when the O content was in the range of 0–7 wt. % because of the presence of fluorapatite, phosphate, hydrogen phosphate, and dihydrogen phosphate. The total phosphate, hydrogen phosphate, and dihydrogen phosphate contents in PAIR exceeded that of fluorapatite, which could be reflected from the P-F correlation scatter plot. The contents of P and F showed two correlation trends, including a positive correlation along the purple line and an irrelevant relationship along the red line. The points with the red line trend showed a significantly higher P content than those with the purple line trend. These results suggest that P existed as phosphate, hydrogen phosphate, and dihydrogen phosphate in the area with a higher P content in PAIR.

**Morphology of fluorine and phosphorus in PAIR**

As shown in Fig. 7, the SEM image of PAIR displayed various morphologies including spherical agglomerate, flake, flocculent and columnar shapes with various. Table 5 lists the EDS results. The one-point substance from the spherical agglomerate was fluorapatite and fluorite. The three-point substance with an indistinct spherical boundary was calcium phosphate, according to elemental analysis. Combined with one-point of analysis, it can be seen that the surface layer of fluorapatite was wrapped by calcium phosphate to prevent the dissolution of fluorapatite, which was also the reason for the presence of fluorapatite in PAIR. The nine-point substance with a smooth square shape was quartz. The four-point smooth plate-like substance was CaF$_2$ produced by reactions (4), (8), and (10). The material on the two-point rough plate was mainly phosphate, hydrogen phosphate, and small amount of fluorides. The five-point short columnar substance was AlPO$_4$. Elemental analysis of flake bodies at eight-points...
and aggregates at six and seven points indicated that these compositions were complex with a high Si content. Therefore, the polymer was composed of AlF$_3$, KF, Al$_{0.35}$Si$_{0.48}$P$_{0.16}$O$_{2.2}$, K$_2$SiF$_6$, and other substances.

**Distribution of fluorine and phosphorus in PAIR**

Figure 8 shows the EPMA surface scan mapping results of the main constituent elements of PAIR. F and P in PAIR were not distributed uniformly, showing a regional agglomeration distribution. Compared to the distribution of other elements, the content of Ca was relatively high in the area with high F and P contents, whereas it was relatively low in areas with Si, O, S, Al, and Fe, as shown in the red box in the figure. These results indicated that the F and P distribution in PAIR strongly correlated with Ca but had a very weak correlation with the other elements. The S content was significantly high in the areas with a high Fe content, as shown in the white box in the figure. The K content was significantly higher in the areas with a higher Al content, as shown in the yellow box in the figure. These results suggest that the distribution of Fe in PAIR has a strong correlation with S, and the distribution of Al had a strong correlation with that of K, which was consistent with the quantitative EPMA analysis results.

Figure 9 shows the simultaneous EPMA surface-scanning mapping of F and P. The red area with only fluorine accounted for 7.74%, while the green area with only phosphorus accounted for 12.19%. The orange area with both fluorine and phosphorus comprised approximately 7.85%. Combined with this figure, the distribution of fluorine and phosphorus in PAIR were partially correlated. Combining the analysis results of the main existing forms of fluorine and phosphorus, it could be determined that the green area mainly represented calcium phosphate, calcium hydrogen phosphate and calcium dihydrogen phosphate, while the orange area represented fluoroapatite and the red area represented...
mainly fluorite and calcium fluoride. The area and depth of the three colors followed the green area > orange area > red area, i.e., 12.19% for P > 7.85% for F-P > 7.74% for F. This showed that the total contents of calcium phosphate, calcium hydrogen phosphate, and calcium dihydrogen phosphate in PAIR were much higher than that of fluorapatite. Furthermore, the content of fluorapatite was higher than that of fluorite and calcium fluoride. These results were consistent with those reflected in the P-F correlation scatter plot shown in Fig. 6.

The formation process of fluorine and phosphorus substances

Combined with the above analysis, Fig. 10 depicts the synthesis of fluorine and phosphorus substances in PAIR during acidolysis. From the figure, the protonation reaction of phosphoric acid produces H⁺, H₂PO₄⁻, HPO₄²⁻, and PO₄³⁻. Apatite dissolves in an acidic environment to form Ca²⁺, PO₄³⁻, OH⁻, and F⁻. A large amount of Ca²⁺ combines with H₃PO₄ to form Ca(H₂PO₄)₂, and a small amount combines with HPO₄²⁻ and F⁻ to form CaHPO₄, Ca₃(PO₄)₂ and CaF₂. Concurrently, K⁺, Mg²⁺ and Al³⁺ are formed from the dissociation of CaMg(CO₃)₂, aluminosilicate and potassium-containing substances. These will react with H₂PO₄⁻, PO₄³⁻ and F⁻ to form KH₂PO₄, KF, Mg₃(PO₄)₂, MgF₂, AlPO₄ and AlF₃. During the reaction of aluminosilicate and phosphoric acid, a small amount of a solid solution compound A₀.₃₅Si₀.₄₈P₀.₁₆O₂.₂ will also be simultaneously formed (Xu et al. 2019). Except for the small amount of SiO₂ that reacts with the intermediate products HF and K⁺ to form K₂SiF₆, the PAIR retains most of the SiO₂ and fluorite. Notably, the insoluble phosphorus (Ca₃(PO₄)₂, etc.) produced during the reaction will wrap around the apatite particles and prevent further acidolysis. This is a significant reason why apatite is still present in PAIR.
Conclusions

The main constituent elements of PAIR were O, Si, Ca, F, P, Al, S, Fe, K, Na, Ti, and Mg, with the total mass ratio of SiO₂, CaO, F, P₂O₅, Al₂O₃, SO₃, and Fe₂O₃ was above 98.14%. The mass fractions of SiO₂, F, and P₂O₅ were 52.708%, 9.407%, and 11.862%, respectively. PAIR is rich in silicon and its fluorine and phosphorus contents have the potential for secondary utilization.

The F and P in PAIR were mainly in the form of fluoroapatite, calcium fluoride, fluorapatite, calcium phosphate, calcium hydrogen phosphate, and calcium dihydrogen phosphate. While small amounts of F and P were present in the form of AlPO₄, KH₂PO₄, Mg₃(PO₄)₂, Al₀.₃₅Si₀.₄₈P₀.₅₆O₂.₂, AlF₃, KF, MgF₂, K₂SiF₆, and organic fluorine. The total phosphate, hydrogen phosphate, and dihydrogen phosphate contents were much higher than those of fluoroapatite. The fluorapatite content was higher than that of fluorine and calcium fluoride.

The F and P in PAIR were not distributed uniformly and showed a strong correlation with the distribution of Ca. F and P were distributed in the form of agglomerates in PAIR. Furthermore, F and P showed a very weak relationship in the high phosphorus area.

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Declarations

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