Applied spectroscopy methods application in the defluorinated phosphate production technological process control problem

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Abstract. The paper considers the applied optical spectroscopy methods application in the defluorinated phosphate production, controlling the technological process task. The emission spectral analysis using the method possibilities to control the charge hydrothermal acid processing process, which takes place in special furnaces with natural gas burning and a temperature of 1340 – 1400°C, have been studied. Experiments have been carried out in production conditions, and the radiation spectral characteristics study results from the furnace during the defluorination technological process are presented. It is shown that, by measuring individual spectral lines, it is possible to provide an automatic control mode for the defluorination technological process in the furnace burner controlling the combustion mode terms without the need for visual observation by the operator to ensure a better product yield. The work second part is devoted to the defluorinated phosphate chemical composition study by the laser-spark emission spectrometry method (LIBS). The LIBS method application for the defluorinated phosphate chemical composition analysis is proposed, which allows the production process parameters real-time control. The plasma spectra measurement and interpretation results from the ready-made defluorinated phosphate sample, obtained using the LIBS method, are presented.

1. Introduction

The technological process essence for the defluorinated phosphate production is the apatite concentrate hydrothermal acid decomposition in the phosphoric acid, caustic soda and a quartz-containing additive presence in rotary kilns. The defluorinated (feed) phosphate production process consists of stages, a number described in [1].

In this process, the most important stage is the charge (defluorination) hydrothermal acid processing, since compliance with technological standards and parameters at this stage greatly affects the resulting product quality.

The charge defluorination process can be described as follows. The pasty charge is sent to the calcining rotary kilns. For calcining the reaction mass, natural gas is burned in furnaces. Due to the furnace rotation and tilt, the charge loaded into the furnace moves along the furnace. Under the high temperatures and incandescent water vapour influence, the blend is defluorinated. The process takes place at 1340-1400°C a temperature. The final product quality is determined by the elements' percentage that makes up the charge and the furnace temperature regime.
During the above-described technological process course, control is carried out at all stages, among which, from the applied optical spectroscopy applying the methods viewpoint [2, 3], the following can be distinguished:

- The combustion process control in the kiln. It is carried out on the indirect parameters measurements basis: temperature and vacuum in furnace various areas, gas flow rate according to the flow meter, the combustion process visual assessment by the operator. The obtained measurement results are compared with the regime maps, on which basis the operator makes decisions on the burner control. The optical spectroscopy methods use will make it possible to control the combustion process in the furnace and, thereby, optimize it in real-time, which will lead to an increase in the fuel combustion efficiency, a decrease in harmful emissions and fuel resource a saving.

- The input raw material composition and the finished product after firing control. Performed in a special laboratory. The content of carbonates and $P_2O_5$ in the apatite concentrate is measured in the raw material, the fluorine, phosphorus and sodium content is measured in the finished product, and the conversion is made to the content of $P_2O_5$. Based on the analysis performed result, a decision is made on the finished product quality. It should be noted that the laboratory analysis procedure takes time a certain amount (about 30 minutes), therefore, if the product quality does not meet the established standards, this leads to the low-quality products a large number release.

In this work, to improve the manufactured product quality and increase the process control speed and reliability, it is proposed to apply the applied optical spectroscopy methods, in particular, optical emission spectroscopy and laser spark emission spectrometry (LIBS).

2. The combustion process in a kiln using optical emission spectroscopy

The technological process for obtaining defluorinated phosphate can be described by the following chemical equation:

$$4Ca_{10}(PO_4)_{6}FOH + 8H_3PO_4 + SiO_2 + 16NaOH = 8Ca_5Na_2(PO_4)_{4} + SiF_4 + 22H_2O \quad (1)$$

Since the process proceeds under the high-temperature influence from the burner flame, chemical element spectral lines present in equation (1) will be observed in the radiation from the furnace. The emission method involves recording the spectrum emitted by an optical radiation source. In the technological process case for the defluorinated phosphate production, the emitted objects are the burner flame used for firing the charge in a rotary kiln, and the fired charge itself.

By measuring the radiation spectrum arising from the defluorinated phosphate production technological process course, it is possible to monitor the ongoing technological process, optimize it and perform some chemical elements a qualitative and quantitative analysis present in the flame and defluorinated phosphate.

The combustion process an experimental study used in the technological process for the defluorinated phosphate production was carried out at a production facility — in a rotary kiln.

Figure 1 shows a rotary kiln photograph installed in the workshop for the GK Fosoforit LLC feed phosphates production, the city of Kingisepp, and the measuring equipment located next to it. A USB2000 + optical spectrometer (1) with a fibrotic probe was used as a measuring device. The forming optics optical axis (2) was directed to the viewing window (3) at the furnace end. The resulting spectrogram was displayed on a computer (4).

The experiment was carried out under the furnace following operating conditions: supplied gas volume 1960 m$^3$/h; pressure 0.40 kg/cm$^2$.

The roasting furnace burner flame obtained spectral characteristic is shown in figure 2.

The radiation spectrum arising from the defluorinated phosphate production technological process course was mainly continuous, which is due to the carbon particles thermal radiation. But at the same
time, 10 spectroscopic informative parameters were observed in the spectrum in the separate spectral lines and bands form, indicated by numbers in figure 2.

Figure 1. The kiln and measuring equipment photo.

Figure 2. Roasting furnace burner flame spectral characteristic.
The results obtained on the flame spectrum measurement with the feed phosphate fertilizer addition to it under laboratory conditions for comparison ease were summarized in Table 1. Based on the reference data [4-11], the obtained spectral lines were compared with chemical elements.

**Table 1.** The flame measuring the spectral characteristics results.

| Spectral lines: \(\lambda_{P1}\) | \(\lambda_{P2}\) | \(\lambda_{P3}\) | \(\lambda_{P4}\) | \(\lambda_{P5}\) | \(\lambda_{P6}\) | \(\lambda_{P7}\) | \(\lambda_{P8}\) | \(\lambda_{P9}\) | \(\lambda_{P10}\) |
|----------------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| Spectroscopic parameters (wavelength, nm) | 330 | 515 | 535 | 563 | 589 | 604 | 616 | 634 | 703 | 770 |
| Chemical element | Na | C_2 | Ca | C_2 | Na | P | Ca | Si | F | K |

The results obtained indicate that the radiation spectrum arising from the defluorinated phosphate production technological process course contains not only parameters characterizing the combustion process but also spectroscopic parameters corresponding to the chemical elements that make up the fired mixture. Therefore, the spectroscopic methods' introduction into this technological process will make it possible not only to control the combustion process to optimize it but also to control the technological process itself.

3. The defluorinated phosphate composition experimental study using the laser spark emission spectrometry method (LIES)

The Laser Spark Emission Spectrometry (LIBS) method is based on the secondary emission spectra measurement produced during plasma formation and evolution when a strong pulsed laser is applied to matter. To obtain a laser spark on the material's surface under study, solid-state Nd:YAG lasers with a switching Q factor and a very short pulse duration are usually used. The short pulses use allows one to avoid significant heat transfer throughout the sample entire volume (only local heating in the laser beam focusing region) and laser radiation screening by the plasma formed at the laser pulse end [12].

To carry out this study, defluorinated phosphate fertilizer a sample was taken in production. This sample was specially selected with a large shape for the experiment convenience.

The experiment purpose was to determine the spectroscopic informative parameters characterizing the finished product composition - defluorinated phosphate.

3.1 The experimental setup description

The experimental setup schematic and photograph for studying the plasma spectrum from the defluorinated phosphate sample are shown in Figure 3.

The experimental setup consists of:

- Lamp-pumped Nd: YAG laser, model LOTIS II 2134U, operating at 1064 nm a lasing wavelength.
- Focusing system for laser radiation, based on an achromatic doublet with an air gap ACA254-150-1064, focal length 150 mm.
- The defluorinated phosphate sample.
- An optical telescope with an attached optical fibre for delivering plasma radiation from the sample understudy to the spectrometer.
- High-speed spectrometers AvaSpec-ULS2048 (working range 255-425 nm) and AvaSpec-3648 (200-900 nm). The two spectrometers use is due to their different spectral measurement ranges. In addition, the AvaSpec-3648 spectrometer has a higher signal-to-noise ratio - 350 instead of 200 for the AvaSpec-ULS2048.
- PC personal computer.

Laser radiation (pulse energy equal to 240 mJ) LOTIS II 2134U is focused on the sample with an ACA254-150-1064 doublet. Plasma radiation is captured by an optical telescope connected to an optical
fibre. In this case, the incident radiation optical axis and the plasma spectrum capture system axis are at a 45 degrees angle.

The plasma radiation then enters the appropriate spectrometer with the AvaSoft software shell through an optical fibre, which measures the plasma radiation spectrum and displays the measurement result on a PC.

![Experimental setup schematic diagram and photograph.](image)

**Figure 3.** The experimental setup schematic diagram and photograph. 1 - Nd: YAG laser LOTIS II 2134U, 2 - ACA254-150-1064 doublet with holder, 3 - defluorinated phosphate sample installed in the holder, 4 - an optical telescope with optical fibre, 5 - spectrometers, 6 - laser control panel.

### 3.2 The Experiment results

In the experiment course, the plasma two emission spectra formed on the defluorinated phosphate sample surface were obtained, measured using two spectrometers with different operating ranges.

Figure 4 shows the plasma radiation spectrum formed on a defluorinated phosphate sample surface, measured with an AvaSpec-ULS2048 spectrometer in the wavelength range of 255 – 425 nm.
Figure 4. Plasma emission spectrum in the frequency range 255-425 nm.

Figure 5 shows a plasma emission spectrum generated on a defluorinated phosphate sample surface measured with the AvaSpec-3648 spectrometer in the wavelength range 200 - 900 nm.

Table 2 shows the spectral element’s most intense lines contained in defluorinated phosphate.

**Table 2.** The elements most intense spectral lines contained in defluorinated phosphate.

| Chemical element | Wavelength, nm          |
|------------------|-------------------------|
| Ca I             | 647.166; 649.378        |
| Ca II            | 315.887; 317.933; 370.603; 373.69; 393.366; 396.847 |
| Ca III           | 421.3144; 422.815; 485.9167; 527.1981; 730.869; 807.421 |
| Mg II            | 279.0776; 279.7998      |
| O II             | 383.029; 384.2815; 407.2157; 615.2566 |
| O-III            | 559.237                |
| P II             | 442.071; 462.67        |
| Na I             | 588.9951               |
Analysing the results obtained, it can be determined that the defluorinated phosphate composition includes magnesium Mg, calcium Ca, oxygen O, phosphorus P, sodium Na. At the same time, the spectral lines corresponding to calcium and sodium have the highest intensity.

4. Conclusion
In this work, to solve the manufacturing defluorinated phosphate technological process control and diagnostics problem, it was proposed to apply the applied optical spectroscopy methods.

The burner flame radiation spectrum in the furnace during the defluorinated phosphate production technological process, as well as the defluorinated phosphate samples spectra, obtained using the laser spark emission spectrometry method, were studied under production conditions.

The results obtained show that the applied optical spectrometry methods can be successfully applied in the manufacturing defluorinated phosphate technological process control problems during a charge firing in a furnace (defluorination process) and the finished product chemical composition control.

The emission spectrum measurement from the furnace during the charge firing allows to optimize the natural gas combustion and, thereby, reduce production costs. In addition, this method use eliminates the need for the operator to visually observe the combustion process in the furnace. For the emission spectrometry method successful application, it is necessary to carry out more large-scale and complex scientific research with the spectroscopic informative parameters statistical data and dependences collection on the raw materials' composition, the furnace operating modes, the final product composition, etc. It is shown that the laser spark emission spectrometry method can be used to control the finished products' composition. The LIBS method has an essential advantage in comparison with laboratory research is the ability to control it in real-time. This allows adjustments to the defluorinated phosphate production process to be made more quickly, which significantly reduces the poor quality products volume.

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References
[1] ITS 19-2016. Manufacturing of solid and other inorganic chemicals. An information technology guide to the best available technology (Moscow: NTD Bureau)
[2] Zaidel A N, Ostrovskaya G V and Ostrovsky Yu I 1972 Spectroscopy technique and practice (Moscow: Nauka)
[3] Tkachenko N V 2006 Optical spectroscopy: methods and instrumentations (Amsterdam: Elsevier)
[4] Arnautov N V, Andreeva L N, Izymova L G and Simonova V I 1965 The main spectral lines reference tables for mineral raw materials semi-quantitative analysis (Novosibirsk, Russia: Acad. Sciences of the USSR. Siberian Branch. Institute of Geology and Geophysics)
[5] Zolotova Yu A, Shekhovtsova T N and Oskolka K V 2017 Analytical chemistry fundamentals (Moscow: Knowledge Laboratory)
[6] Gaydon A G 1950 Spectroscopy and combustion theory (Moscow: IL)
[7] Fedorov A A et al. 1974 Phosphorus analytical chemistry (Moscow, Russia: Nauka)
[8] Myshlyaeva L V and Krasnoshechekov V V 1972 Silicon analytical chemistry (Moscow, Russia: Nauka)
[9] Korenman I M 1964 Potassium analytical chemistry (Moscow: Science)
[10] Borzov S M et al. 2017 The Kolibri-2 spectrometer' use to study the flame radiation/ and others Factory laboratory Materials diagnostics 83(7) 13-8
[11] Toro C et al. 2020 On the detection of spectral emissions of iron oxides in combustion experiments of pyrite concentrates Sensors 20(5) 1284
[12] Kremers D and Radziemski L 2009 Laser-spark emission spectroscopy (Moscow: Technosphere)