

## RESEARCH ON SORPTION PROPERTIES OF PHOSPHORIC PRODUCTION SLAG-WASTE

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On the territory there are phosphorus-containing wastes - phosphorus slags, the basis of which is volostanite. The study of phosphorus slag as a uranium sorbent is of theoretical and practical interest. In the course of the research, comparable data were obtained on the sorption of the initial and activated slag by different reagents. The optimal conditions for the activation of phosphorus slag in order to increase its sorption properties have been determined.

*Keywords:* uranium-containing waste, phosphorus slag, X-ray research, sintering, activation

### INTRODUCTION

Kazakhstan occupies a leading position in the structure of world production of uranium, which is produced using an environmentally friendly method of in-situ leaching. However, the presence of uranium-containing waste from large hydrological provinces and small deposits is a dangerous source of contamination of natural waters with radionuclides, due to the large volumes and the possibility of uncontrolled spread. The best option for their disposal has not yet been found; this problem remains a key issue for the nuclear industry. Sorption is the most common way of liquid radioactive waste (LRW) disposal.

Sorption is the most common method for disposal of liquid radioactive waste. Despite the high results achieved in the sorption of uranium by synthetic ion exchangers, their wide use for the disposal of liquid radioactive waste (LRW) is hindered by their high cost. In addition, an important problem is the lack of its own production of synthetic sorbents in the republic. Recently, much attention has been paid to modified ion exchange materials. Phosphorus-containing modified sorbents have proven themselves well [1-2], but they are effective only when used by small industries.

In this regard, natural ion-exchange materials, the reserves of which are estimated in millions of tons, as well as technogenic mineral formations with sorption properties, deserve special attention for LRW disposal. Among technogenic raw materials, special attention should be paid to slags of phosphorus production, the main component of which, according to preliminary data, is wollastonite, which has sorption properties. The objective of the research was to study the effect of the composition and structure of phosphorus slag on the sorption of ura-

nium, as well as the effect of chemical reagents on it in order to increase the sorption properties.

### RESEARCH METHODS

The phosphorus slag was activated in a thermostated reactor at an optimum temperature of 85 °C in solutions of sodium carbonate and chloride. The concentration of sodium carbonate varied from 100 to 200 g/dm<sup>3</sup>, sodium chloride - from 50 to 200 g/dm<sup>3</sup>, and the duration of the process from 2 to 6 hours; the solid-to-liquid ratio was 1:5. Further experiments on the activation of phosphorus slag at the same concentrations of carbonate and sodium chloride, as well as the duration of the process and the solid-to-liquid ratio were carried out in an autoclave. The temperature varied in the range 150 - 230 °C. Test experiments on the sorption of uranium were carried out in a static mode at room temperature. The solid-to-liquid ratio of 1: 100. The uranium concentration in the productive solution was 17,7 mg/dm<sup>3</sup>.

### ANALYSIS METHODS

The quantitative content of uranium in solutions before and after sorption was determined on an Optima 8300DV inductively coupled plasma atomic emission spectrometer (ICP). Solid samples were analyzed by X-ray phase, X-ray fluorescence, mineralogical methods of analysis and energy-dispersive spectrometry. IR spectra were obtained on an Avatar 370 CsI FT-IR spectrometer in the spectral range of 4 000-300 cm<sup>-1</sup> from preparations in the form of a tablet prepared by pressing 2 mg of a sample and 200 mg of KBr.

### RESULTS AND ITS DISCUSSION

Phosphorus slag is a waste product from the phosphorus industry. According to preliminary physico-

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chemical studies, the main phase of the phosphorus slag - calcium silicate - is represented by the amorphous phase of wollastonite, which exhibits pronounced sorption properties. At the same time, the analysis of publications in the scientific literature devoted to the synthesis and transformations of calcium silicates showed that at elevated temperatures and pressures, as a rule, changes in their structure occur, which affects the sorption properties [3-7]. A significant number of publications are devoted to the hydrothermal method. The hydrothermal method has several advantages. In particular, it provides ample opportunities for obtaining particles that are uniform in composition, shape, and size [3-4].

The hydrothermal method is implemented at elevated temperatures in thermostated reactors, as well as under conditions of elevated temperatures and pressures using autoclave equipment [5-7]. These conditions simulate the processes of formation of minerals in the earth's interior. As the aqueous phase, calcium salts and sodium chloride are usually used.

Thus, the hydrothermal treatment of phosphorus slag, under certain conditions, will make it possible to influence its structure, and hence its properties, including sorption ones.

In this regard, our research is devoted to the physicochemical study of the composition of phosphorus slag, transformation of its structure at elevated temperature and pressure, determination of the optimal activation conditions by hydrothermal treatment and the sorption properties of activated phosphorus slag. Table 1 shows the chemical composition of the slag sample, from which it follows that.

The main constituents of the slag are Si, Al, Ca, Mg; Fe and P are present in smaller amounts, which is also confirmed by mineralogical analysis and energy dispersion spectrometry (magnification x1 000) (Figure 1).

According to the X-ray phase method, the basis of the slag is an amorphous phase, the crystalline phase contains: Calcite –  $\text{Ca}(\text{CO}_3)$  – 66,85 %, Calcium Oxide Silicate –  $\text{Ca}_3(\text{SiO}_4)\text{O}$  – 19,64 %, Ankerite –  $\text{Ca}(\text{Fe}+2\text{Mg})(\text{CO}_3)_2$  – 8,29 %, Iron Silicon ( $\text{Fe}_{0,9}\text{Si}_{0,1}$ ) – 5,23 %.

Mineralogical analysis established that the sample is more than 90 % represented by amorphous mineral phases with different refractive indices. The amorphous phase with a refractive index of about 1,615-1,625, which is close to natural wollastonite, predominates. A small amount contains crystalline phases of carbonates - calcite and ankerite, as well as calcium oxide silicate and iron silicate. Phosphorus is believed to be present as lazulite.

Thus, the main phase of the phosphorus slag is amorphous, attributed to isotropic artificial wollastonite glass phase, partially crystalline in the form of carbonates and silicates.

Hydrothermal treatment of phosphorus slag was carried out according to the conditions described above. The research results showed that during the hydrothermal treatment of phosphorus slag with sodium carbonate, its structure changes: the amorphous phase under-

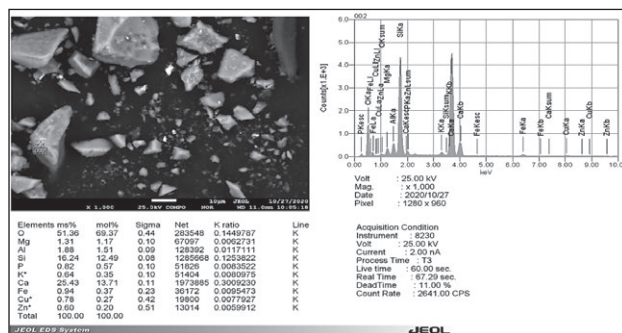


Figure 1 Results of point analysis of energy-dispersion spectrometry of the initial sample of phosphorus slag

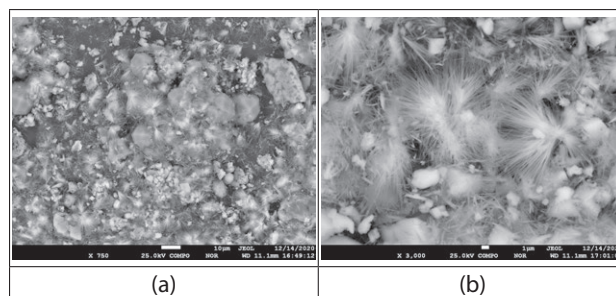


Figure 2 Particles of activated ( $\text{Na}_2\text{CO}_3$  - 150 g/dm<sup>3</sup>,  $t^\circ$  - 230 °C) force slag with an increase in: a - x750 (a) and x 3 000 (b)

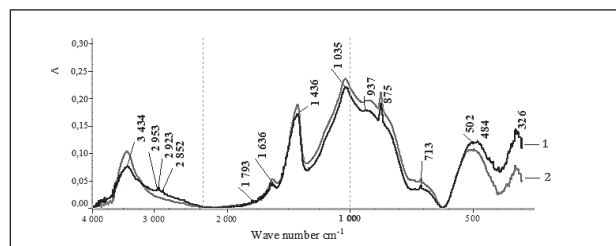


Figure 3 IR spectrum of the initial (1) phosphorus slag and activated with sodium chloride (2)

goes changes, transforming into a crystalline one, and the changes are noticeable already after two hours of hydrothermal treatment at a temperature of 85 °C (Table 2). With an increase in temperature and duration of the process, the changes are more pronounced. As the temperature rises, the morphology of the particles also changes: the conglomerates existing in the initial sample gradually change their shape and turn into acicular particles (Figure 2). At the same time, the concentration of sodium carbonate, in the studied limit, does not significantly affect the phase composition of the activated phosphorus slag and the structure of its particles.

A completely different picture is observed during the hydrothermal treatment of phosphorus slag with sodium chloride. According to X-ray phase analysis, there is no sharp change in the phase composition of the slag. The amorphous structure of the slag is retained even at elevated temperatures.

Thus, during the hydrothermal treatment of phosphorus slag with sodium carbonate, its phase composition and structure change, and upon treatment with so-

Table 1 **Chemical composition of phosphorus slag**

| Product name    | Content/% |                                |                  |                               |       |                                |
|-----------------|-----------|--------------------------------|------------------|-------------------------------|-------|--------------------------------|
|                 | MgO       | Al <sub>2</sub> O <sub>3</sub> | SiO <sub>2</sub> | P <sub>2</sub> O <sub>5</sub> | CaO   | Fe <sub>2</sub> O <sub>3</sub> |
| Phosphoric slag | 3,597     | 5,496                          | 37,133           | 1,214                         | 34,25 | 2,002                          |

Table 2 **Change in the phase composition of phosphorus slag in the process of activation.**

| Method for activating phosphorus slag                                | Compound Name               | Formula  | %    |
|--|-----------------------------|--|------|
| Na <sub>2</sub> CO <sub>3</sub> – 150 g/dm <sup>3</sup> , t° – 85°C  | Calcite, magnesian, syn     | (Mg <sub>0,06</sub> Ca <sub>0,94</sub> )(CO <sub>3</sub> ) | 100  |
|  | Calcite, syn                | Ca(CO <sub>3</sub> )                                       | 57,5 |
|  | Analcime-M                  | NaAl(Si <sub>2</sub> O <sub>6</sub> )(H <sub>2</sub> O)    | 20,4 |
| Na <sub>2</sub> CO <sub>3</sub> – 150 g/dm <sup>3</sup> , t° – 230°C | Ankerite                    | Ca(Fe+2Mg)(CO <sub>3</sub> ) <sub>2</sub>                  | 14,9 |
|  | Aluminum Phosphide          | AlP  | 4,7  |
|  | quartz, syn   Silicon Oxide | SiO <sub>2</sub>   | 2,4  |

Table 3 **The degree of sorption of uranium by phosphorus slag, activated by different methods**

| Raw materials   | Reagent concentration upon activation/g/dm <sup>3</sup> | Activation temperature/°C | Residual uranium content/mg/dm <sup>3</sup> | Uranium sorption degree/% |
|-----------------|---|---------------------------|---|---------------------------|
| Phosphoric slag | -   | -                         | 5,7   | 67,9                      |
|                 | Na <sub>2</sub> CO <sub>3</sub> – 150                   | 150                       | 7,2   | 59,1                      |
|                 | Na <sub>2</sub> CO <sub>3</sub> – 150                   | 230                       | 7,4   | 58,3                      |
|                 | NaCl – 50   | 85                        | 4,5   | 74,5                      |
|                 | NaCl – 150  | 85                        | 4,1   | 77,1                      |
|                 | NaCl – 100  | 230                       | 0,1   | 99,5                      |

Table 4 **Results of the study of activated phosphorus slag by X-ray fluorescence analysis**

| Raw materials   | Activation options     |      | Metal content/% |      |       |      |       |      |
|-----------------|------------------------|------|-----------------|------|-------|------|-------|------|
|                 | NaCl/g/dm <sup>3</sup> | t/°C | Mg              | Al   | Si    | K    | Ca    | Fe   |
| Phosphoric slag | -                      | -    | 1,15            | 1,54 | 15,97 | 0,36 | 24,64 | 0,84 |
|                 | 50                     | 85   | 1,07            | 1,39 | 14,68 | 0,28 | 23,27 | 0,71 |
|                 | 100                    | 85   | 1,01            | 1,31 | 13,7  | 0,37 | 22,72 | 0,68 |
|                 | 200                    | 85   | 0,97            | 1,30 | 13,6  | 0,31 | 21,94 | 0,67 |

dium chloride under the same conditions, the main amorphous phase is retained.

In this regard, the study of the sorption of uranium by the hydrothermal activated phosphorus slag is of certain theoretical and practical interest.

The studies were carried out according to the method described above. The research results showed (Table 3) that uranium is more actively sorbed by phosphorus slag, activated by sodium chloride.

In order to explain this phenomenon, we carried out studies of phosphorus slag, activated with sodium chloride, by the IR spectroscopic method (Figure 3).

IR - spectroscopic analysis of the sample showed the presence of bands in the spectrum at wave numbers 1 039, 922, 754, 497 cm – 1, corresponding to multicomponent glass [8]. The band at 1 039 cm – 1 refers to the

stretching vibrations of the Si – O – Si bonds, and the band at 922 cm – 1 to the stretching vibrations of the terminal Si – O – bonds [9].

The fixed shift of the maximum of the band of stretching vibrations of the terminal Si – O – bonds of glass to the high-frequency region up to 937 cm – 1, with a decrease in the Fe<sub>2</sub>O<sub>3</sub> content relative to the initial slag, indicates a change in the composition of the glass and corresponds, for example, to the idea of the authors [10] about the participation of Fe cations <sup>+3</sup> in the glass grid.

Thus, Fe<sup>3+</sup> cations are involved in the construction of a mixed iron – silicon – oxygen framework. When the slag is activated with a sodium chloride solution, the content of iron ions in the framework decreases. Such defects contribute to an increase in the degree of sorption of uranium by phosphorus slag. The data obtained were confirmed by X-ray fluorescence analysis (Table 4). It follows from the table that during the activation of the slag with sodium chloride, there is a decrease in the content of not only iron, but also, in small amounts, calcium, magnesium, aluminum and silicon. Taking into account the research data [5], the resulting “voids” can easily be filled with sorbed ions, for example, uranium.

## CONCLUSION

The composition of phosphorus slag, which is a waste of phosphorus production, has been studied by the methods of physicochemical research. It is shown that the main phase of the slag is close to natural wollastonite. A small amount contains crystalline phases of carbonates - calcite and ankerite, as well as calcium oxide silicate and iron silicate. Phosphorus is believed to be present as lazulite.

In the course of research, it was found that when the slag is activated by sodium carbonate by the hydrothermal method in a wide temperature range, it transforms from the amorphous phase to the crystalline phase. In addition, the morphology of the slag particles changes. When activated with sodium chloride, no significant changes in the phase composition of the slag were noted. According to the results of IR spectroscopic analysis, Fe<sup>3+</sup> cations are involved in the formation of a mixed iron-silicon-oxygen framework of the phosphorus slag. When the slag is activated with a sodium chloride solution, the content of iron ions in the framework decreases. The content of magnesium, calcium, aluminum and silicon also decreases, according to X-ray fluorescence analysis. Such defects contribute to an increase in the degree of sorption of uranium by phosphorus slag.

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Wave number cm<sup>-1</sup>

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**Note:** The responsible translator for the English language is D. Imankulova, JSC “KBTU”, Kazakhstan