DETERMINATION OF PRODUCTS OF CHEMICAL REACTION BETWEEN ALKALI METALS AND ALKALINE EARTH METALS TETRAFLUOROBROMATES AND METALLIC IRIDIUM

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ОПРЕДЕЛЕНИЕ ПРОДУКТОВ ВЗАИМОДЕЙСТВИЯ ТЕТРАФТОРОРОМАТОВ ЩЕЛОЧНЫХ И ЩЕЛОЧНОЗЕМЕЛЬНЫХ МЕТАЛЛОВ С МЕТАЛЛИЧЕСКИМ ИРИДИЕМ

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В данном исследовании была показана принципиальная возможность проведения первого этапа выделения благородных металлов из городских отходов, а именно, их гомогенизации и перевода в растворимые формы на примере металлического иридия с использованием тетрафторобромата щелочных и щелочноземельных металлов. Определён состав получаемых продуктов, предложена схема протекания реакций и уточнены условия начала реагирования. Предложенный метод может лечь в основу способа перевода благородных металлов в растворимые формы и последующего выделения из вторичного сырья.

Nowadays there is a rising interest for noble, rare and rare-earth metals extraction and separation from the urban wastes [1, 2]. Despite the noticeable number of the research works devoted to this problem, the universal solution has not been found yet.

One of the directions of modern methods is the conversion of the compounds of precious metals into simple or complex fluorides and their further separation.

In the present research work the possibility of using relatively poorly studied class of fluorine compounds - alkali and alkaline earth metal tetrafluorobromates - was investigated. The purpose of this paper is to show how this class of compounds react with one of the noble metals - metallic iridium and what products can be obtained.

All experiments were carried out in the dry box under argon atmosphere. The interaction between iridium and tetrafluorobromates was carried out in vacuum-sealed fluorine-passivated nickel ampoules. The samples were pelleted in advance. The ampoules were heated in a muffle furnace up to 400 °C for 120 minutes, then maintained at this temperature for 150 minutes, next 240 minutes they were cooled slowly.

The diffraction study was done on Stadi-P diffractometer (Stoe, Germany) using CuKα radiation with a germanium monochromator and a Mythen1K detector. Further powder pattern processing was carried out in Jana2006 software [3].

The first sample represents the products obtained after the reaction with a large excess of tetrafluorobromate Ir:$KBrF_4$=1:12 (mass.). The diffraction study was done by means of X-ray powder diffraction. The corresponding X-ray powder pattern is shown in the Figure 1. The pattern peaks of the obtained substance were compared with the corresponding peaks from diffraction database PDF-2 [4]. The sample mainly consisted of

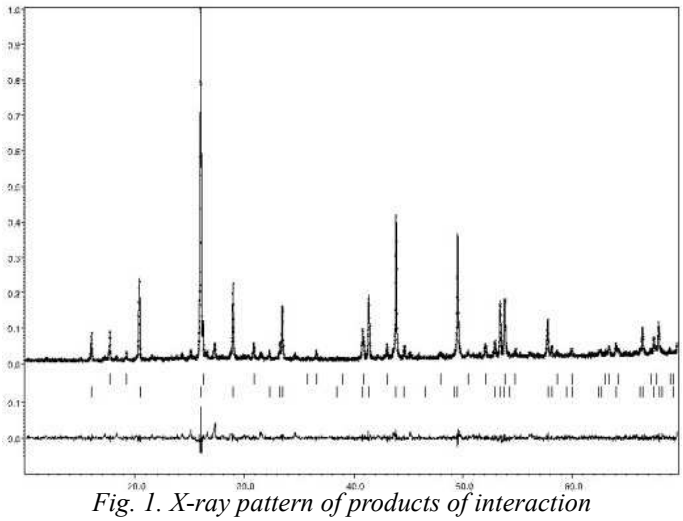


Fig. 1. X-ray pattern of products of interaction Ir:$KBrF_4$ = 1:12 (mass.)R_n = 0,1047, R_{wn} = 0,1487

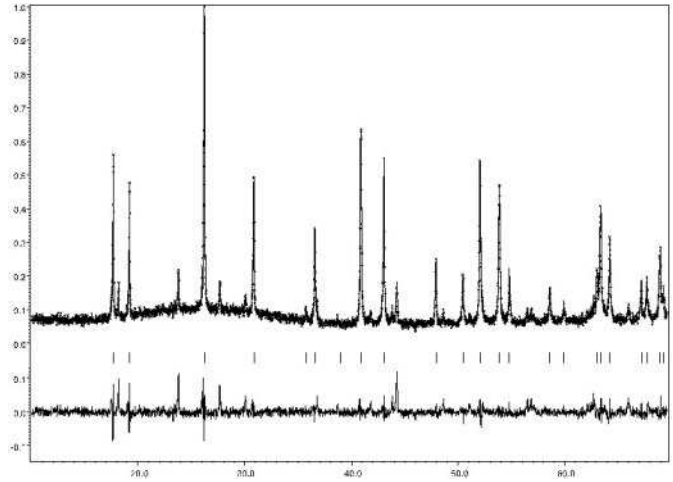


Fig. 2. X-ray pattern of products of interaction Ir:$KBrF_4$ = 1:2 (mol.)Rp = 0.0884, Rwp = 0.1230

two products: potassium hexafluoroiridate K_2IrF_6 and the unreacted excess of potassium tetrafluorobromate $KBrF_4$. Based on these data, it was suggested that the reaction proceeds according to the following scheme:

$$Ir + 2KBrF_4 \rightarrow K_2IrF_6 + 2BrF\uparrow$$

The stoichiometric interaction of iridium and potassium tetrafluorobromate (Ir:$KBrF_4$ = 1:2 mol.) was also investigated. However, the results of powder X-ray diffraction showed the presence of potassium tetrafluorobromate (Figure 2). This is probably due to the establishment of thermodynamic equilibrium between starting materials and products after the reaction is completed in a confined space.

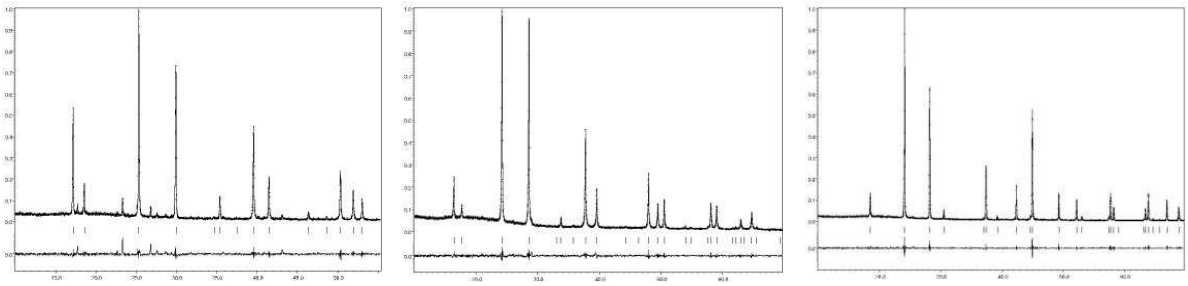
In case of lack of the fluorinating agent, for instance Ir:$KBrF_4$=1:1 (mass.) ratio, there are hexafluoroiridate and metallic iridium in the mixture after the reaction. In addition, the pattern has some peaks that belong to some unidentified substances.

For investigation of the fundamental possibility of interaction between metallic iridium and other tetrafluorobromates such as $RbBrF_4$, $CsBrF_4$ и $Ba(BrF_4)_2$ the series of experiments were carried out. The stoichiometric amounts of the reactants were calculated using the following equations:

$$Ir + 2RbBrF_4 \rightarrow Rb_2IrF_6 + 2BrF\uparrow$$

$$Ir + 2CsBrF_4 \rightarrow Cs_2IrF_6 + 2BrF\uparrow$$

$$Ir + 2Ba(BrF_4)_2 \rightarrow BaIrF_6 + 2BrF\uparrow$$



а) Rb_2IrF_6 *б) Cs_2IrF_6* *в) $BaIrF_6$*

R_p = 0.0945, R_{wp} = 0.1422 *R_p = 0.0516, R_{wp} = 0.0696* *R_p = 0.0641, R_{wp} = 0.0837*

Fig. 3. X-ray patterns of the products of the stoichiometric interaction of metallic iridium with cesium, rubidium and barium tetraflurobromates.

In all samples the formation of the corresponding metal hexafluoroiridate was observed. In case of rubidium

tetrafluorobromate there are also peaks which belong to rubidium fluoride, because some amount of fluoride was present in the initial tetrafluorobromate as am impitiry. As for cesium and barium tetrafluorobromates, the admixtures were not found. The obtained X-ray powder patterns are shown in the Figure 3.

This investigation shows the fundamental possibility of carrying out the first stage of extraction of noble metals from the urban wastes with alkali and alkaline earth tetrafluorobromates, namely, their homogenization and dissolution by the example of metallic iridium. The composition of the products was obtained, a scheme of reactions was proposed. The initial conditions of the reaction were clarified.

The proposed method can form the basis for transferring the precious metals to soluble forms and the subsequent extraction from the wastes. Future research works will be dedicated to the separation of metals from their mixtures and composites.

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FLUORORAMMONIUM COMPLEX COMPOUNDS OF RARE EARTH METALS OF TYPE (NH_4LnF_4)

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ФТОРАММОНИЙНЫЕ КОМПЛЕКСНЫЕ СОЕДИНЕНИЯ РЕДКОЗЕМЕЛЬНЫХ МЕТАЛЛОВ ТИПА (NH_4LnF_4)

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Рассмотрены термохимические процессы синтеза и разложения фтораммонийных комплексов редкоземельных металлов. Методом дифференциальной термической калориметрии определены температурных максимумов скорости образования и разложения комплексных соединений и определены величины кажущейся энергии активации процессов.