Synthesis of Potassium and Calcium Uranovanadates, analogues of Carnotite and Metatyuyamunite Minerals

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The aim of this study was to develop a synthesis of metatyuyamunite ($Ca(VUO_6)_2 \cdot 3\text{-}5H_2O$) and carnotite ($KVUO_6 \cdot 1\text{-}3H_2O$) under hydrothermal conditions. Also, crystals obtained from this synthesis were compared with crystals from melting method. The analyses of synthesis products were performed by X-Ray techniques. X-Ray Diffraction was used for both species identification, whereas Scanning Electron Microscopy was used to analyze their morphology and elemental composition. Both uranovanadates were positive synthesized under hydrothermal conditions; besides, their morphology presents particles agglomerates. Calcium uranovanadate agglomerates contain well-defined crystals, whereas potassium uranovanadate agglomerates consist in fine powder particles.

Keywords: Uranium; carnotite; metatyuyamunite; hydrothermal synthesis; crystallization.

El objetivo de este trabajo fue desarrollar una ruta de síntesis de metatyuyamunita ($Ca(VUO_6)_2 \cdot 3\text{-}5H_2O$) y Carnotita ($KVUO_6 \cdot 1\text{-}3H_2O$) en condiciones hidrotermales. Los cristales obtenidos de estas síntesis se compararon con cristales obtenidos por el método de fusión. El análisis de los productos de las síntesis fue realizado mediante técnicas de rayos X. La difracción de rayos X fue utilizada para la identificación de las dos especies, mientras que la Microscopía Electrónica de Barrido se utilizó para analizar su morfología y composición elemental. Ambos uranovanadatos fueron exitosamente sintetizados bajo condiciones hidrotermales, presentando una morfología de aglomerados de partículas. Los aglomerados del uranovanadato de calcio están formados por cristales bien definidos, mientras que los aglomerados del uranovanadato de potasio consisten en partículas de polvo muy finas.

Descriptores: Uranio; carnotita; metatyuyamunita; síntesis hidrotermal; cristalización.

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1. Introduction

Metatyuyamunite and carnotite are two minerals commonly found in uranium ores like in Utah-Colorado and Sonora, Texas [1,2]. They belong to a wide class of inorganic compounds with uranium and vanadium called uranovanadates of alkali and alkaline-earth metals. Karyakin *et al.,* [3,4] after a theoretical thermodynamic study, suggested a relatively simple and well reproducible route of uranovanadates synthesis using crystalline uranovanadic acid as ion-exchange matrix. Moreover, it is also documented that it is necessary to prepare uranyl pyrovanadate before obtaining the uranovanadic acid [5].

The Victorino and San Marcos I uranium deposits are located near to Chihuahua city, in the State of Chihuahua, Mexico. In a recent study it was concluded that the San Marcos I uranium deposit was formed by hydrothermal mineralization [6]. Besides, metatyuyamunite ($Ca(VUO_6)_2 \cdot 3\text{-}5H_2O$) is one of the species observed there. It is also well known that carnotite ($KVUO_6 \cdot 1\text{-}3H_2O$) is a compound commonly mixed with metatyuyamunite [7]. The elevated uranium content in Victorino and San Marcos I ores is of great scientific and environmental interest, because in this zone runs the San Marcos River that is a tributary of Sacramento River. Furthermore, Sacramento River is one of the most important water source for agricultural and other economical activities in Chihuahua City [8].

Nowadays, uranium has special importance because of its raising use mainly as a fuel in nuclear plants. In consequence a growing scientific interest in understanding its migration in environment and the correct disposal of uranium-containing wastes promote the study of its mineral species. In spite of the foregoing, the crystal chemistry of uranium minerals lags well behind than many other minerals groups. At the moment, one third of the known uranium species have been determined and refined [9].

It is well known that physical and chemical properties of a compound are closely related to its crystalline structure. The crystallization of a mixture of many components will produce crystals that are purer than the starting material. Hence crystallization is frequently used as an energy-efficient way to purify a material. The size and shape of crystals determine physical and chemical properties, such as strength and solubility and are also important in many applications. Furthermore, crystallography is capable of providing detailed information on molecular structures as interatomic distances and bond angles, among others.

The word hydrothermal is specially used in Geology to describe the formation of minerals from hot solutions rising from a cooling magma. Likewise, hydrothermal synthesis is defined as any heterogeneous reaction in aqueous media above 100°C and 1 bar [10]. Besides, this method is also used for growing crystals [11]. On the other hand, the most frequently used and important method to produce bulk single crystals of a given material is by solidification of its own melting [12]. Its technical and economic importance is due to the fact that large single crystals can be grown very efficiently.

In a previous work, the crystal structure from a natural metatyuyamunite sample was determined [13]. In that study, the sample was extracted from the Peña Blanca ore, which is close to San Marcos area. The applied method was a Rietveld refinement of a powder diffraction pattern of the natural sample. In order to achieve better structures for both carnotite and metatyuyamunite, we have been studying the synthesis of crystals large enough for refining the structure using single crystal X-ray diffraction. To reach this aim, a significant size of the pure compound is required. Hence, the objectives of this study were first, to develop a synthesis of metatyuyamunite ($Ca(VUO_6)_2 \cdot 3\text{-}5H_2O$) and carnotite ($KVUO_6 \cdot 1\text{-}3H_2O$) under hydrothermal conditions and second, to grow crystals as a final part of these synthesis. Furthermore, potassium uranovanadate crystals should be obtained by melting method for comparing them with those obtained by hydrothermal conditions.

2. Materials and methods

The study was performed in the Advanced Materials Research Center (CIMAV) located at Chihuahua City, Mexico. Two routes of synthesis to obtain potassium and calcium uranovanadates under hydrothermal conditions were explored. The first route of synthesis involves a previous preparation of uranyl pyrovanadate, and the second one was the direct potassium and calcium uranovanadate synthesis.

X Ray Diffraction (XRD) was used to identify the obtained species in products; this technique was performed using a Panalytical X'Pert PRO MPD. Scanning Electron Microscopy with Energy Dispersive of X-Ray (SEM-EDX) was used to analyze morphology and particle composition for both uranovanadates A JEOL JSM5800-LV microscope at 15 kV with acquisition of digital images in both secondary (SEI) and backscattered (BEI) electron imaging modes coupled with the EDS EDAX DX prime was used.

The potassium uranovanadate melting point was determined by DTA analysis, using SDT 2960 simultaneous DTA-TGA equipment. Images for potassium uranovanadates crystals obtained by melting method were taken by an OLIMPUS SZH-10 polarizing microscope.

Uranyl pyrovanadate synthesis

Uranyl pyrovanadate was prepared by a solid reaction [5] A stoichiometric amount of vanadium pentoxide (J.T. Baker) and uranyl acetate (SPI-CHEM) with a 10% excess were crushed in agate mortar, adding acetone. This mixture was dried at 80°C. After that, the sample was calcined at 760°C during three days in a platinum crucible This temperature was reached at the rate of 3°C min^{-1}.

Potassium and calcium uranovanadates hydrothermal synthesis using uranyl pyrovanadate previously prepared

The K and Ca uranovanadates were prepared mixing appropriates quantities of the uranyl pyrovanadate previously prepared, and KOH or $Ca(OH)_2$ (J.T. Baker) in a 10% excess. This mixture was crushed in agate mortar with 5 mL redistilled water. The pH of the resulting solution was adjusted to 2-3 with concentrated HCl (J.T. Baker). The reactants were heated in a 23 mL Teflon-lined Parr bomb at 150°C for 5 days. The following reactions took place [3,4]

$$\begin{aligned} K^+(\text{aq}) + 1/2\ \ (UO_2)_2V_2O_7\ \ (\text{cr}) \\ + 1/2\ \ H_2O\ (\text{l}) \rightarrow KVUO_6\ \ (\text{cr}) + H^+(\text{aq}) \\ Ca^{2+}(\text{aq}) + (UO_2)_2V_2O_7\ \ (\text{cr}) \\ + H_2O\ (\text{l}) \rightarrow Ca(VUO_6)_2\ \ (\text{cr}) + 2H^+(\text{aq}) \end{aligned}$$

Direct potassium or calcium uranovanadate hydrothermal synthesis

For these syntheses the reactants used were stoichiometry amounts of vanadium pentoxide (J. T. Baker), uranyl acetate (SPI-CHEM), KOH or $Ca(OH)_2$ (J.T. Baker) and 5 mL redistilled water. The pH of the resulting solution was adjusted to 2-3 with concentrated HCl (J.T. Baker). The reactants were heated in a 23 mL Teflon-lined Parr bomb using isothermal bath oil at 220°C during 48 h.

Potassium uranovanadate crystallization by melting method

After the potassium uranovanadate synthesis a Thermogravimetric Analysis (TGA) determined its melting point. Potassium uranovanadate was molten in a platinum crucible in an inert atmosphere. The temperature was increased in a 3°C min^{-1} rate until 1,200°C was reached. This temperature was sustained during 2 min and then it was descended in a $15^\circ\text{C min}^{-1}$ rate to room temperature.

Synthesis products validation using XRD modeling

All experimental XRD patterns obtained from the synthesis products were compared with a pattern modeled with Powdercell 2.4 software. Uranyl pyrovanadate and potassium uranovanadate charts were taken from Inorganic Crystal Structure Database, numbers ICSD No. 79308 and ICSD No. 64692, respectively.

Calcium uranovanadate model pattern was taken from the Rietveld refinement given in reference [13].

3. Results and discussion

Uranyl pyrovanadate synthesis

The synthesis product was analyzed by XRD and the results confirmed the presence of uranyl pyrovanadate (Fig. 1). The

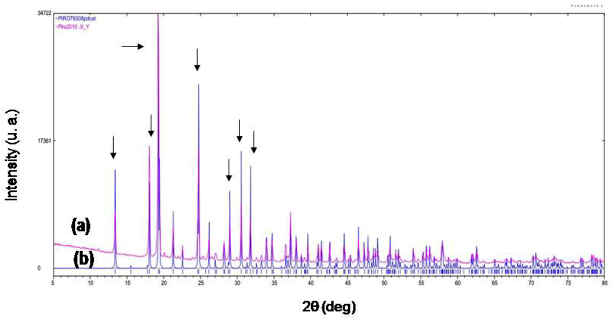

FIGURE 1. Powder X-ray Diffraction uranyl pyrovanadate patterns. Experimental pattern is shown as a) whereas the modeled one from ISCD No. 79308 card is shown as b). Arrows show main diffraction peaks characteristic of uranyl pyrovanadate pattern.

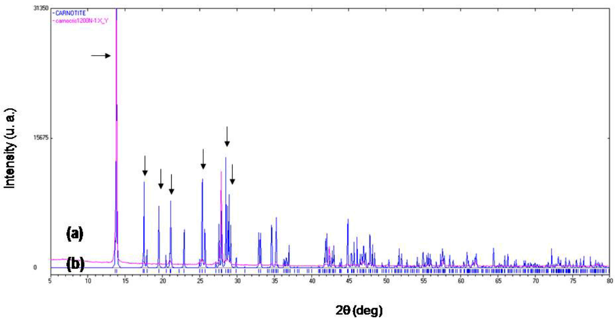

FIGURE 2. Powder X-ray Diffraction potassium uranovanadate patterns. Experimental pattern is shown as a), whereas the modeled one from the ISCD No. 64692 card is shown as b). Arrows show main diffraction peaks characteristic of potassium uranovanadate pattern.

first time this synthesis was done, the X-ray powder diffractogram showed not only the uranyl pyrovanadate phase, but also vanadium pentoxide. This feature was interpreted as an indicator of the limiting reactant role of uranyl acetate in the reaction. A 10% excess of uranyl acetate was used and the vanadium pentoxide was not present on subsequent XRD powder patterns.

Potassium and calcium uranovanadates hydrothermal synthesis using uranyl pyrovanadate previously prepared

Both potassium and calcium uranovanadates were prepared at the same time, in such a way that a better reaction conditions analysis was done for each synthesis

The first potassium and calcium synthesis were performed at 150°C during 24 h. The XRD patterns from these products showed the desirable phases but also uranyl pyrovanadate and other intermediate reaction products as impurities. Uranyl pyrovanadate found on products analysis was an indicator for a limiting reactant presence in the reaction; likewise the intermediate products were a non-completed reaction indicator Afterwards, both $Ca(OH)_2$ and KOH were added with a 10% excess. Furthermore, time reaction was increased to 5 days in order to reduce intermediate reaction products. As a result, non-significative impurities quantity and consequently better reaction efficiency were obtained.

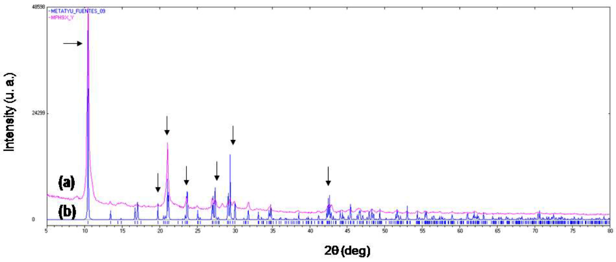

FIGURE 3. Powder X-ray Diffraction calcium uranovanadate patterns. Experimental pattern is shown as a), whereas the modeled from Burciaga *et al.* [13] is shown as b) Arrows show main diffraction peaks characteristic of calcium uranovanadate pattern.

Direct potassium or calcium uranovanadate hydrothermal synthesis

This route of synthesis reduces the preparation time at least 48 h, time needed for uranyl pyrovanadate preparation. Furthermore, the utilization of purer reactants increases the product quality. Time and temperature were changed in order to optimize the reaction conditions; as a result a final 220°C temperature was determined. Rising temperature produces the same effect as a reaction long time: it increases the reaction efficiency. Hence, rising reaction temperature results in a synthesis time reduction from 5 days to 48 h without compromising the product quality. Moreover this synthesis route offers a very simple method for preparing both potassium and calcium uranovanadates, without previous uranyl pyrovanadate preparation. Powder XRD analysis was used to confirm the presence of potassium and calcium uranovanadates, Fig. 2 and Fig. 3, respectively.

SEM applied to uranovanadates samples

SEM technique was used to analyze potassium and calcium uranovanadates. The images show agglomerates formed by particles of different sizes from 100 to 500 nm with very irregular form.

General morphology of uranovanadates is presented in Fig. 4. It can be observed that both potassium and calcium uranovanadates show agglomerates at the same magnification (Fig. 4a and 4b). A detailed image for the agglomerates structure is shown in Fig. 4c and 4d, where differences are observed. Potassium uranovanadate agglomerates of Fig. 4c are formed by fine powder particles, whereas calcium uranovanadate agglomerates are formed by crystals with angular shapes like flakes (Fig. 4d). In Fig. 4e and 4f a better perception of particle morphology is obtained, where calcium uranovanadate (Fig 4f) presents well-formed crystals, in contrast with potassium uranovanadate (Fig. 4e), which shows powder particles.

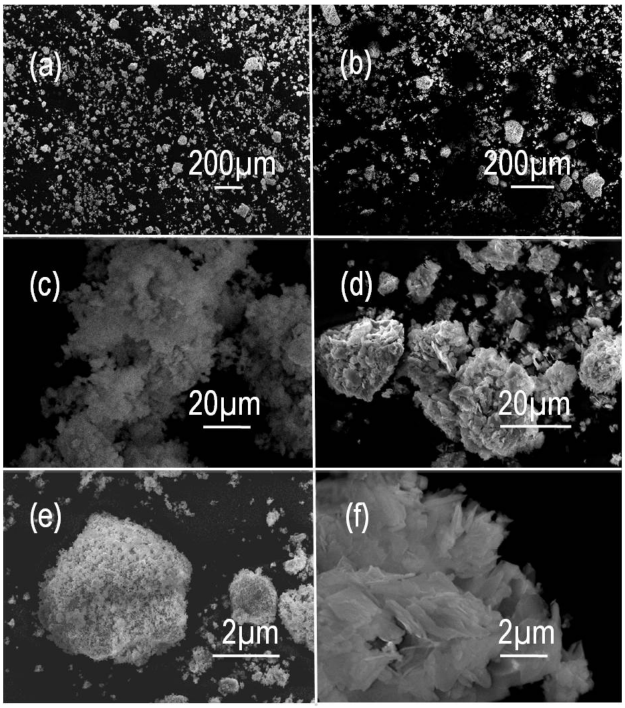

FIGURE 4. SEM images of calcium and potassium uranovanadates samples obtained by hydrothermal synthesis. Images a), c) and e) correspond to potassium uranovanadate, whereas images b), d) and f) show calcium uranovanadate Images a) and b) were obtained at 90X magnification images c) and d) at 1500X magnification, whereas images e) and f) correspond to 10 000X magnification.

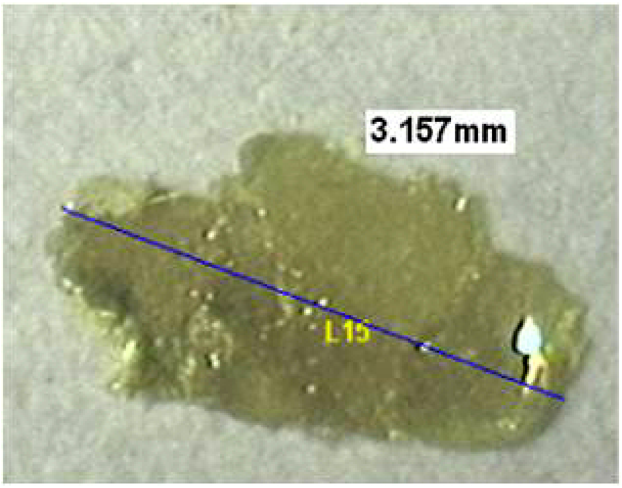

FIGURE 5. Potassium uranovanadate crystal obtained by Melting Method with approximately 3.2 mm length.

The EDX results for elemental composition were for potassium uranovanadate: K, U, V and O, whereas for calcium uranovanadate: U, V, Ca and O. These technique results agreed with Powder XRD results.

4. Potassium uranovanadate crystallization by melting method

The melting method for potassium uranovanadate crystallization results in large crystals as Fig. 5 shows. The obtained crystals were bright yellow; however crystallization results in bulked crystals without the desirable morphology according with these work objectives.

5. Conclusions

The potassium and calcium uranovanadates were positive synthesized under hydrothermal conditions and the uranyl pyrovanadate and uranovanadic acid precursors were also successfully prepared. Notable advantages result from direct synthesis: it requires less preparation time, beside this direct reaction reduces the reactants manipulation. Furthermore, instead a reactant previously prepared as uranyl pyrovanadate, the high quality reactants utilization results in a high purity product. It is recommended to continue this type of studies, to improve the hydrothermal synthesis conditions for achieving larger crystals. Changes in the synthesis condition into alkaline media and longer time for crystallization may be explored.

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