

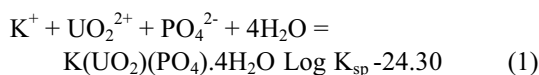
# The Removal of Uranium From Aqueous Effluents via Meta-Ankoleite Formation

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## 1. Introduction

It is known that many metal phosphate salts possess low solubilities. Uranium is no exception with many uranium/uranyl phosphate minerals having very low solubilities.[1] In recent years the formation of insoluble uranium phosphates, such as Meta-Ankoleite (1), have been researched for the effective sequestering of environmentally mobile uranium.[2]



In this study we have investigated the suitability of dosing mono-potassium phosphate (MKP,  $\text{KH}_2\text{PO}_4$ ) for the selective removal of uranium from a complex, highly contaminated, waste effluent (Table 1). The effluent in question is generated as part of the treatment strategy for a legacy uranium catalyst waste which has been in temporary storage since 2004 in Korea.[3]

A range of both pH (3 – 11) and phosphate dosages (0.25 – 10 mM) have been screened. Precipitation kinetics has also been investigated revealing the effectiveness of phosphate addition for the rapid removal of uranium from solution in less than two hours.

The effluent was decontaminated via meta-ankoleite formation, as confirmed by XRD, to uranium levels below the compulsory release limit of 1 ppm. Final decontamination factors of the order of  $\geq 10^3$  were readily achieved thus ensuring that the effluent meets the Korean release criteria for U-bearing liquid waste.

## 2. Experimental

### 2.1 Materials

All materials were used as received. MKP ( $\text{KH}_2\text{PO}_4$ , 99.5%) was obtained from SHOWA, potassium hydroxide (KOH, 85%) from JUNSEI and nitric acid ( $\text{HNO}_3$ , 65%) from MERCK. The effluent was produced during the treatment of the uranium catalyst and stored in 20 L plastic drums before use.[3]

### 2.2 Method

A known aliquot of the effluent was placed into a 50 mL beaker and stirred at 180 rpm with a magnetic stirrer bar. MKP was added to reach the required concentration (0.25 – 10 mM). KOH was added until the desired pH was reached (3.0, 5.0, 5.5, 6.0, 6.25, 6.5, 7.0, 8.0, 9.0 or 10.5) and allowed to react for two hours. For the kinetic testing solution samples were taken at 1, 2, 4, 8, 16, 30, 60 and 120 minutes and prepared for ICP-OES analysis.

All solution samples were filtered through a 0.2  $\mu\text{m}$  syringe filter and acidified with 5 %  $\text{HNO}_3$  before being analysed via ICP-OES (Analytikjena PQ9000 Elite).

Upon completion of the reaction the precipitates were collected, centrifuged and washed with de-ionised water (18.2 M $\Omega$ , 5 x 50 mL) to remove the remaining  $\text{Na}_2\text{SO}_4$  which is present in the effluent stream (Table 1). The washed precipitates were then dried and analysed via SEM/EDX (Bruker Namo, Xflash Detector 410-M) and XRD (Bruker D2 Phaser).

Table 1. Summary of effluent parameters as received

pH	Conductivity <sup>1</sup> (mS/cm)	TSS (ppm)	Turbidity (NTU)	Particle size <sup>2</sup> ( $\mu\text{m}$ )	[U] (mM)	[Si] <sup>3</sup> (mM)	[Sb] <sup>3</sup> (mM)	[Ca] <sup>3</sup> (mM)	[Mo] <sup>3</sup> (mM)	[SO <sub>4</sub> <sup>2-</sup> ] (M)	Ionic strength (M)
0.85	101.7	200	237	17.2	0.09	3.62	0.44	0.40	0.27	0.37	1.14

<sup>1</sup> Measured at a constant 25.0 °C, <sup>2</sup> Mean volume measure, <sup>3</sup> Elements with [mM] greater than uranium (Al, Cu, Fe, Zn, B, Ni and Cr present  $\leq 0.09$  mM)

### 3. Results & Discussion

#### 3.1 pH Screening

Fig. 1 shows the concentration of uranium remaining in solution at a range of pH values after two hours, with and without the addition of  $\text{KH}_2\text{PO}_4$  (1 mM). The addition of phosphate is clearly effective for the removal of U when compared to no phosphate addition with an optimal pH of 6.00 – 6.50. Uranium is removed independently of silicon at the target pH.

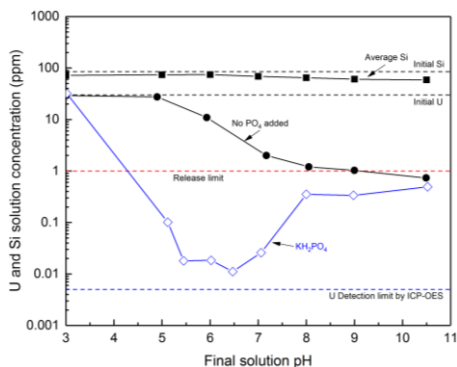


Fig. 1. Results from the pH screening tests.

#### 3.2 Dosage & kinetics screening

Fig. 2 shows the results of the dosage screening as a function of time. A  $\text{KH}_2\text{PO}_4$  concentration of 1 mM or greater is needed in order to achieve the required release limit with 2 mM being found as optimal.

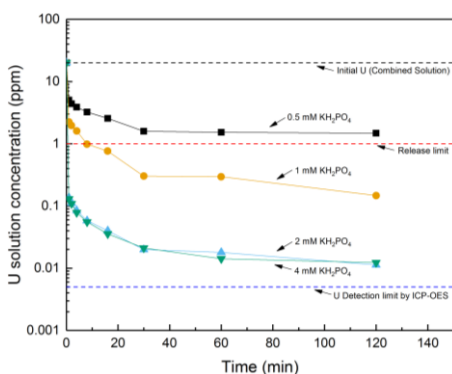


Fig. 2. Results from the phosphate dosage screening.

Further addition of phosphate does little to enhance the removal of uranium and would only lead to complications further down the process with the requirement of excess  $\text{PO}_4^{3-}$  removal.

#### 3.3 Meta-Ankoleite characterization

The formation of the Meta-Ankoleite mineral phase was confirmed by XRD (Fig. 3). This is in agreement

with previous experimental data presented by M. Kanematsu *et al.*[2]

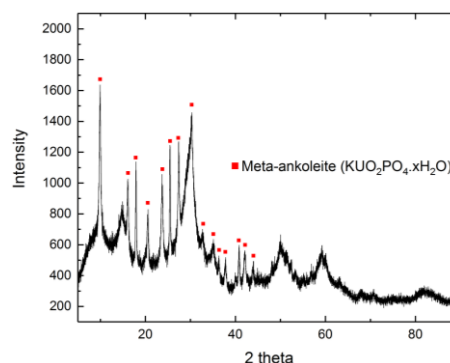


Fig. 3. XRD analysis result of the collected precipitates.

SEM analysis (Fig. 4) indicates the formation of amorphous precipitates approximately 10 – 100  $\mu\text{m}$  in size. Elemental mapping indicates the presence of both Si and Sb suggesting co-precipitation is occurring. The chemical composition of Si and Sb is unknown.

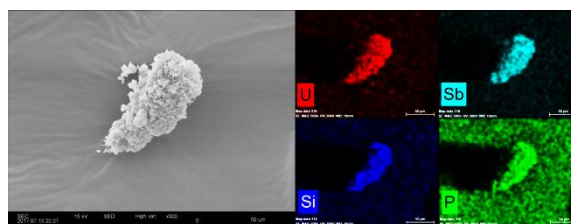


Fig. 4. SEM image with accompanying elemental map.

### 4. Conclusions

The addition of MKP to the effluent has been found effective for the selective removal of uranium as the Meta-Ankoleite mineral phase.

Parameter screening has enabled process optimization to a pH (6.25), dosage (2mM) and kinetics (1hr), for a final [U] of < 20 ppb.

The process will now enter bench and pilot testing phases. Residual phosphate requires a removal strategy, e.g.  $\text{FeCl}_3$ , before final release.

### REFERENCES

- [1] D. Gorman-Lewis *et al.*, "Review of uranyl mineral solubility measurements", *J. Chem. Thermodynamics*, 40, 335-352 (2008).
- [2] M. Kanematsu, N. Perdrial *et al.*, "Influence of Phosphate and Silica on U(VI) Precipitation from Acidic and Neutralized Wastewaters", *Environ. Sci. Technol.*, 48, 6097-6106 (2014).
- [3] K. W. Kim *et al.*, "The development of a process for the volume reduction of uranium catalyst waste used for production of acrylonitrile", *In Press* (2017).