Formation of Meta-Ankoleite for the Decontamination of Uranium Bearing Effluents: From Laboratory to Pilot Plant

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1. Introduction

In a number of recent publications, we have characterized a uranium containing spent catalyst waste and detailed a process for the treatment of this waste.[1-3] As part of the process the formation of Meta-Ankoleite (KUO₂PO₄.4H₂O), during one of two precipitation steps, is used to remove uranium and decontaminate the effluent. Previously, our Meta-Ankoleite precipitation studies have focused on laboratory scale testing (10-100 mL).[3] In this paper, we wish to communicate the steps taken and results obtained since going from the Laboratory to Pilot Plant (1000 L), via Bench Scale (1 - 3 L), and discuss the problems and challenges faced. A full description of the waste, steps taken for treatment and proposed Meta-Ankoleite formation method can be found in pervious publications.[1-3]

2. Experiment

2.1 Materials

All materials were used as received. For laboratory and bench scale tests, mono-potassium phosphate (MKP, KH₂PO₄, 99.5%) was obtained from SHOWA, KOH (85%) from JUNSEI. For the Pilot Plant, MKP (90%) and KOH (90%) were used. In all cases nitric acid (65%) was obtained from Merck. All ICP dilutions were performed with deionised water (18 MΩ). Full details of the target effluent are in ref 1-3.

2.2. Method

To a known volume of effluent MKP was dosed while being mixed resulting in a total $[PO_4^{3-}]$ of between 1 – 4 mM. The solution was then adjusted to the target pH by the addition of KOH. Stirring was maintained throughout the experiment. The resulting suspended Meta-Ankoleite was removed via a filter press. The solution was then passed through a pleated filter before "final release". Solution analysis took place before and after precipitation and after both filters. Analysis consisted of ICP-OES, TSS, NTU, PSA, pH, EC and ORP measurements. SEM/EDS, XRD and XRF analysis of the formed solids were also performed.

3. Results and discussion

3.1 Optimal laboratory conditions

At the outset of this project phosphate was dosed in the form of MH_2PO_4 (M = Na, K or NH_4). According to reported solubilities, the NH_4 counter ion should yield the greatest uranium removal, followed by K and Na. This was confirmed to be the case although the difference between the lowest [U] was only 11, 18 and 38 ppb for NH₄, K and Na, respectively, at pH 6. Due to concerns with the decomposition of $NH_4(UO_2)(PO_4)$ during thermal solidification the K form, Meta-Ankoleite, was chosen. Dosage and kinetics measurements confirmed a concentration of 1 mM for a period of 60 minutes was sufficient for the removal of uranium (Table 1).[3]

Table 1. Optimized laboratory conditions for Uranium removal

pН	Ion	Dosage	Stir speed	Time	Final [U]
6.25	K^+	1 mM	100 rpm	60 min	20 ppb

3.2 Bench scale testing and process refinement

The transition to bench scale was not without its problems. Initial tests revealed that the optimized laboratory conditions traversed well. However, the effluent used had aged which was unrepresentative of the real system which does not allow for a prolonged aging period (> 24 hr). Subsequent tests with fresh effluent revealed a slower rate of kinetics. It has been concluded that effluent aging allows for the formation of particulate Sb-oxides which aid in the rapid removal of uranium via seeding. Regardless, all test conditions lead to a removal of uranium to below the release limit; although an increase of phosphate dosage to 2mM was found optimal.



Fig. 1. Uranium removal kinetics at bench scale. Bench_01 and Bench_02 performed with aged effluent at a $[PO_4^{3-}]$ of 1 and 2 mM, respectively. Bench_03 and Bench_04 performed with fresh effluent at a $[PO_4^{3-}]$ of 1 and 2 mM, respectively.

3.3 Pilot Plant

3.3.1 Meta-ankoleite formation. Regulatory restrictions prohibited the use of the real waste catalyst during pilot scale tests. In order to test the whole process a simulant was proposed for the silica precipitation stage; the resulting effluents were to be

treated at the phosphate precipitation stage (**Table 2**). A 1000 L stainless steel tank with a two tier quadbladed stirrer was used. The incoming effluent totaled approx. 220 L, containing 28 ppm U.

Table 2. Pilot plant simulant effluent (ppm)

Contaminant:	U	Si	Sb	Mo	Fe	Al	Mg
Initial simulant	200	20,000	1800	300	30	30	20
Effluent	28	107	38	44	6	4	20

A total phosphate concentration of 2 mM was used. The pH was adjusted to 6.2 which drifted only slightly to 6.4 over 1 hour. The formation of lemon-yellow precipitates, also indicated by a change in turbidity, was almost instantaneous. The formed precipitates were confirmed to be meta-ankoleite by XRD and chemical analysis (**Table 3**). The analysis results matched well with the previous smaller scale tests, thus indicating that the process can be scaled.

Table 3. Meta-ankoleite chemical analysis

	U	K	Р	Si	Sb	Mo	Fe	Al	LE
Pure	58.8	9.6	7.7	-	-	-	-	-	23.7
Simulant	14.5	7.7	1.2	2.7	15.5	-	1.1	-	40.0

The precipitates were allowed to settle for one hour before filtration, although settling was seen to have occurred within 10 min by visual inspection. While the particles are small, approx. 10 μ m [3], they possess a high density resulting in fast settling times.

3.3.2 Filtration. Working at pilot scale gave rise to the opportunity to test a number of filtering scenarios. Filtering was done with a filter press, with and without a filter aid, and also via a pleated filter. While the use of no filter aid afforded the fastest filtration rates these quickly retarded due to filter membrane blockages. The use of a filter aid affords greater filtration rate consistency. Opting to only filter the supernatant yielded the best filtration rate. Results indicate a single pass through a pleated filter is sufficient (**Table 4**). Allowing the particles to settle prior to supernatant filtering is the preferred method.

Table 4. Summary of effluent U concentrations after filtration.

		Time (minutes)					
Filter	Press	1	2	4	8	16	30
Without	Bulk	5.8	2.7	0.9	0.2	0.1	0.09
filter aid	Supernatant	1.2	1.2	0.8	0.8	-	-
F :1	Bulk	2.8	1.8	0.7	0.4	0.4	0.07
r mer ala	Supernatant	0.4	0.3	0.3	0.3	-	-
Pleated filter		1 st		2^{nd}	3 ¹	d	4^{th}
	Supernatant	0.12	2	0.10	0.0)7	0.06

3.3.3 Process comparisons. The physical and chemical properties of the treated effluents and solids are summaries in table 5. **Green** values meet release criteria while **Red** values need to be addressed further.

Black values have no direct regulatory consequence. Principally, all three experimental scales meet the release requirement with regard to uranium. All other parameters are similarly comparable indicating a consistency in the process. A removal method for the residual TSS and $[PO_4^{3-}]$ is required with both precipitation, by FeCl₃, or ion-exchange, for PO_4^{3-} , being actively considered.

	Maaaaa	Lab	Bench	Pilot	
	Measurement	scale	scale	Plant	
	[U] Initial (ppm)	20	20	28	
	[U] Final (ppb)	20	5	63	
	DF^1	1111	4000	444	
	[P] Final (ppm)	16	18	50	
tior	TSS ² (ppm)	282	194 ³	-	
olu	Turbidity (NTU)	0.2	0.5 ³	0.5 ³	
S	Particle size (µm)	63.1	53.8	10.0	
	pН	6.00	6.19	6.4	
	EC ⁴ (mS/cm)	-	58	-	
	ORP ⁵	-	514	-	
	Floc volume (mL/L)	16.7	12.5	-	
olic	Solid volume (mL/L)	0.08	0.10	-	
Ś	VRF^{6}	12540	10000	-	

Table 5. Summary of solution and solid analysis

4. Conclusions

Over three experimental scales the removal of uranium via meta-ankoleite formation has been tested. Both laboratory and bench scale tests made use of the real effluent which was effectively decontaminated. Due to regulator restrictions the real waste could not be used at the pilot plant, thus limiting the pilot plant tests to a simulant. Nonetheless, the results were in good agreement with previous smaller scale tests. It was therefore accepted that the removal of uranium via the formation of meta-ankoleite was successful over all three tested experimental scales. The complete process is now in the process of being up-scaled to a commercial scale plant. A PO_4^{3-} removal method is still required, with FeCl₃ dosing preferred.

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