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IMPROVED URANIUM RECOVERY FROM THE PROCESS STREAMS IN AN ELECTROPLATING FACILITY

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IMPROVED URANIUM RECOVERY FROM THE PROCESS STREAMS IN AN ELECTROPLATING FACILITY*

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ABSTRACT

Cylindrical uranium slugs are used as irradiation targets in the production reactors at the Savannah River Plant. These slugs are first chemically etched, nickel plated, encased in aluminum, inspected, and individually pressure tested. An improved process was developed to recover the uranium from the acidic etching streams by controlling pH and the PO_4 to U ratio so that the precipitation of the uranium as hydrogen uranyl phosphate was maximized. Bench scale tests demonstrated that the recovery of uranium could be increased to greater than 99.9% (vs. the current level of about 95% recovery). The recommended changes involved the addition of process effluent "hold" tanks. The addition of the various process streams to the neutralization/precipitation tank could therefore be controlled to maintain a consistent ratio of uranyl nitrite and phosphoric acid. Also, it was determined that a strong caustic solution (resulting from the dissolution of rejected aluminum slugs) could be utilized to neutralize the nitric and phosphoric acid solutions. The buffering action of the aluminum in the "caustic recovery solution" would reduce the sensitivity of the hydrogen uranyl phosphate precipitation to the phosphate ion concentration.

INTRODUCTION

The fuel and target elements used in the SRP production reactors at the Savannah River Plant (SRP) are prepared in the fuel fabrication facilities (300-M Area). Depleted uranium is used for the target elements, and after irradiation, the product plutonium is separated in the Separations facilities (200-F Area).

The target elements consist of hollow cylinders, approximately 8-1/4 inches long and 3 inches in diameter, with about 1/2-inch-thick walls. The uranium cores are received from NLO, Inc., Fernald, Ohio, and processed through an automated plating line. The cores are first etched in a strong (6 N) nitric acid solution to remove the oxidized surface. The cores are then anodically etched in a strong phosphoric acid (17 N)/hydrochloric acid (0.5 N) solution to prepare the surface for the subsequent nickel plating operations. The phosphoric/hydrochloric acid solution is removed with a nitric acid rinse prior to the nickel plating. The nickel plated cores are encapsulated in aluminum, inspected, and pressure tested to ensure the integrity of the aluminum cladding before emplacement in the reactor.

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The plating line solution process is a batch-type operation, with the spent solutions being transferred to a solution recovery operation. Each of the acidic solutions is dumped when its dissolved uranium concentration becomes too high for effective use. For example, the initial nitric acid pre-etch tank is dumped when the uranyl nitrate reaches a concentration of approximately 300 g/L. The spent acidic solutions are combined and neutralized with sodium hydroxide. The resulting precipitate is filtered, with the filter cake going to low-level waste burial, and the filtrate being released to a surface impoundment. This system normally recovers about 95% of the uranium in the spent solutions.

In 1983, a program was initiated by the Savannah River Plant to try to improve the percent recovery of the uranium. Use of slightly enriched uranium feed material (~1% U^{235}) for the target elements (vs. depleted uranium, ~0.20% U^{235}) was being considered. However, since the slightly enriched material is more radioactive than the depleted material, and since the geometry of the enriched cores had more surface area, the amount of radioactivity released to the settling basin would have exceeded the Du Pont-SRP operating guidelines. The value of the recovered enriched uranium was also significant, at approximately 190/kg.

This work defined the precipitation chemistry pertinent to the process conditions, and developed process modifications which, if implemented, were predicted to improve the uranium recovery to >99.9%.

EXPERIMENTAL METHODS

Samples of actual process solutions were used for all experiments. The acidic solutions were neutralized to the desired pH and mixed until a uniform dispersion was obtained. A sample of the slurry was vacuum filtered through No. 42 Whitman filter paper. The filtrates were analyzed by a direct current argon plasma spectrometer.

RESULTS AND DISCUSSION

The experimental results indicated that the maximum precipitation of uranium occurred at a pH of 6.0 ±1.0 (Figure 1). An extensive x-ray spectrophotometric investigation of the precipitate showed that hydrogen autenite [1 (hydrogen uranyl phosphate - $H_2(UO_2)_2(PO_4)_2 \cdot 8H_2O$) was the primary precipitate] in that pH range. $HUO_2PO_4 \cdot 4H_2O$, $NaUO_2PO_4$ and $(UO_2)_3(PO_4)_2 \cdot 4H_2O$ were also found. The chemistry of the precipitation process is quite complex, with more than 30 chemical equations contributing to the overall reaction. Two of the primary reactions [2,3] are the pH sensitive precipitation of HUO_2PO_4,

$$(UO_2)(NO_3)_2 + H_3PO_4 \rightleftharpoons HUO_2PO_4\downarrow + 2HNO_3 \tag{1}$$

and a complexing reaction in which excess phosphate redissolves the HUO_2PO_4 precipitate:

$$HUO_2PO_4 + HPO_4^{=} \rightleftharpoons UO_2(HPO_4)_2^{=} \tag{2}$$

The calculated optimum pH for uranium precipitation, considering only these two reactions, would be about 4.0. However, these tests, using actual process solutions containing phosphate, chloride, nitrate, uranium, aluminum, nickel, sodium, and other trace elements, consistently demonstrated a pH of about 6.0 for maximum precipitation.

The data plotted in Figure 1 also indicate the effect of differing phosphate to uranium ratios. It is apparent that at higher mole ratios of PO_4:U the amount of the soluble uranium complex increases, with the resulting uranium concentration in the filtrate increasing from approximately 25 ppm at a PO_4:U molar ratio of 2-4:1 to >500 ppm at a molar ratio of 10-15:1.

It was found that using a very strong caustic recovery solution containing aluminum (~100 g/L) would buffer the phosphate complexing reaction, thereby reducing the sensitivity of the process to excess phosphate (Figure 2). This is caused by a competing precipitation of $AlPO_4$, which also has its minimum solubility in the 5.5 to 7.0 pH range [4]. Comparing the data in Figures 1 and 2 indicates that significantly less soluble uranium is present at the higher phosphate ratios when the core recovery caustic solution (containing aluminum) is used to neutralize the acidic solutions (vs. using sodium hydroxide alone).

The order of mixing of the strong acid and caustic solutions has a significant effect on the precipitation sequence. For maximum precipitation (minimum uranium in the filtrate) the caustic solution should be added to the acid solution so that the pH increases to the desired 5-7 range. Data showing the effect of starting the precipitation with a large caustic excess vs. starting at a low pH are given in Figure 3. Initiating the neutralization at a high pH allows sodium diuranate ($Na_2U_2O_7$) to initially precipitate [5,6] as shown in Equation 3:

$$2UO_2(NO_3)_2 + 6NaOH \rightleftharpoons Na_2U_2O_7\downarrow + 3H_2O + 4NaNO_3 \qquad (3)$$

According to Metzger and Heidelberger [7] the sodium diuranate may be initially precipitated, but it undergoes partial hydrolysis, resulting in a sodium uranate with the composition $Na_4U_5O_{17}$. The overall reaction is shown in Equation 4:

$$5UO_2(NO_3)_2 + 14NaOH \rightleftharpoons Na_4U_5O_{17}\downarrow + 7H_2O + 10NaNO_3 \qquad (4)$$

These uranate or diuranate precipitates are more soluble than the hydrogen uranyl phosphate material precipitated at the lower pH. Theoretically, the more soluble uranates should redissolve as the pH is reduced from 11-12 to the 5 to 6 range, and the more insoluble uranyl phosphates would precipitate. However, the data in Figure 3 indicate that this does not happen quickly. Allowing the solutions to equilibrate for 48-72 hours does allow the more soluble uranium solution to transform to the less soluble situation.

SUMMARY AND CONCLUSIONS

Laboratory tests demonstrated that the key parameters controlling the recovery of uranium from the plating line process effluent streams were pH and phosphate to uranium ratio. A number of surge tanks were designed to hold the various process tank dumps so that controlled amounts of each of the different process solutions would be released to the neutralization/precipitation stage. In addition, it was recommended that the core recovery caustic solution, which had previously been discharged as waste, be utilized to neutralize the acidic solutions (instead of fresh NaOH). This not only

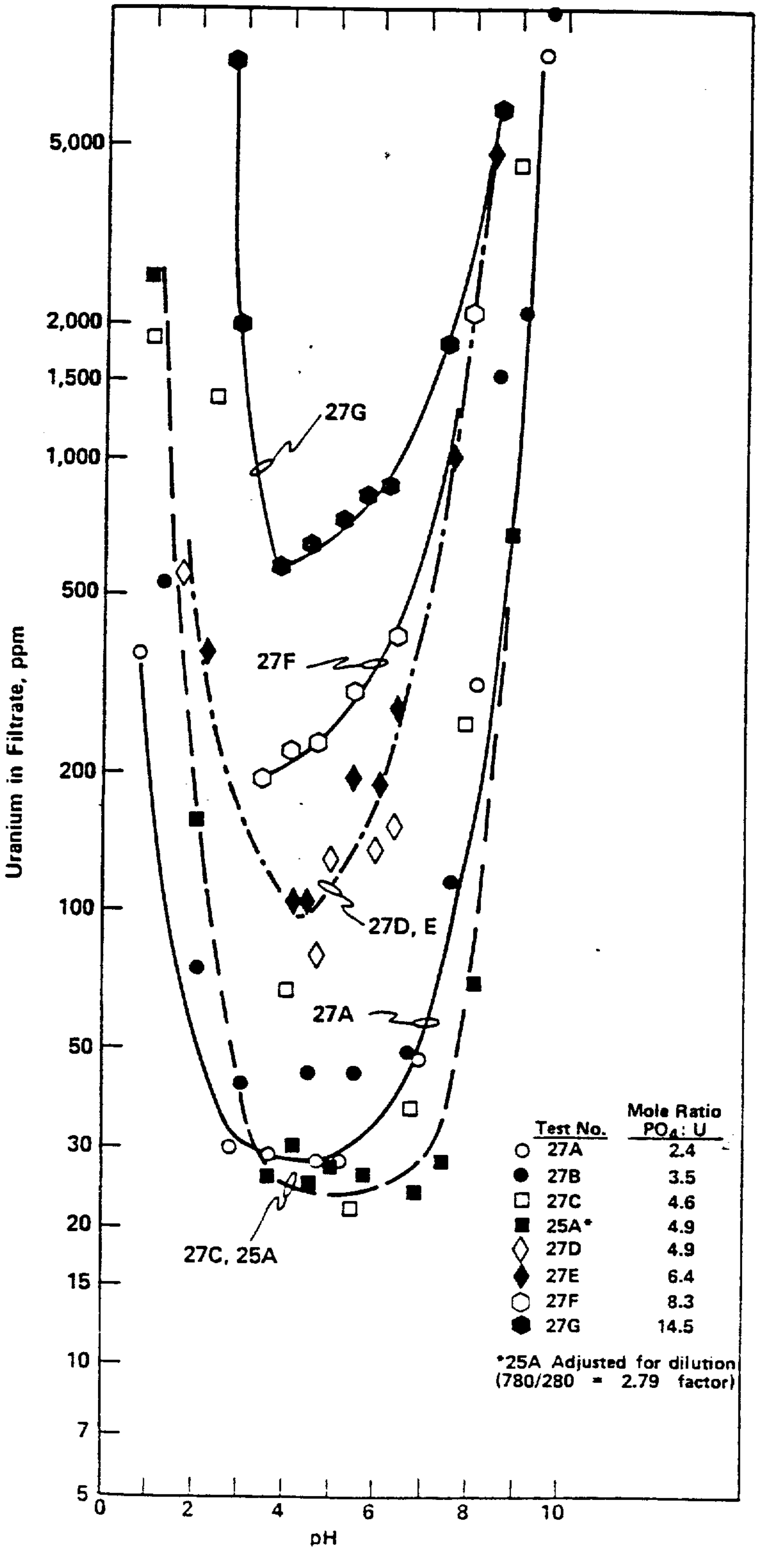

FIG. 1. Concentration of Uranium in Filtrate (ppm) vs. pH and PO_4^{-3}:U Ratio. NaOH Used to Neutralize.

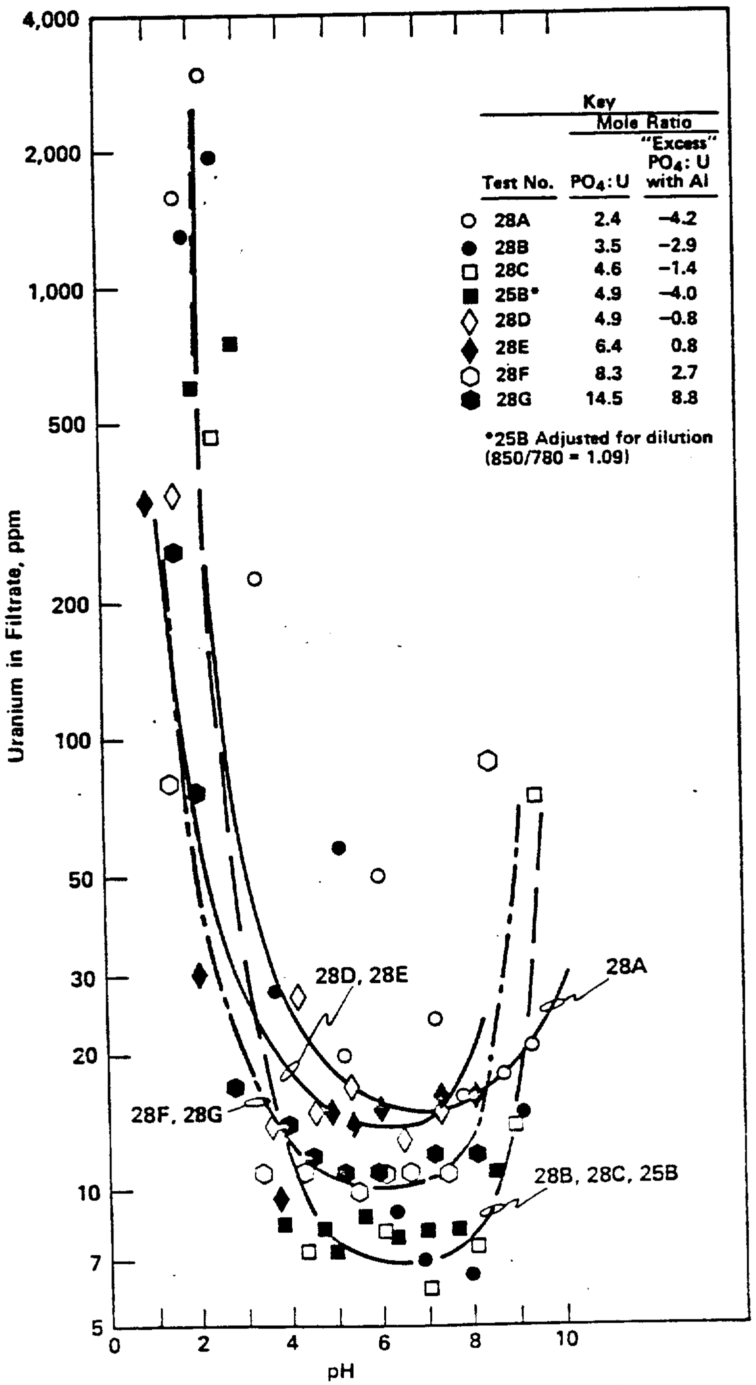

FIG. 2. Concentration of Uranium in Filtrate (ppm) vs. pH and PO_4^{-3}:U Ratio. A Core Recovery Caustic Solution Containing Al^{+3} Used to Neutralize.

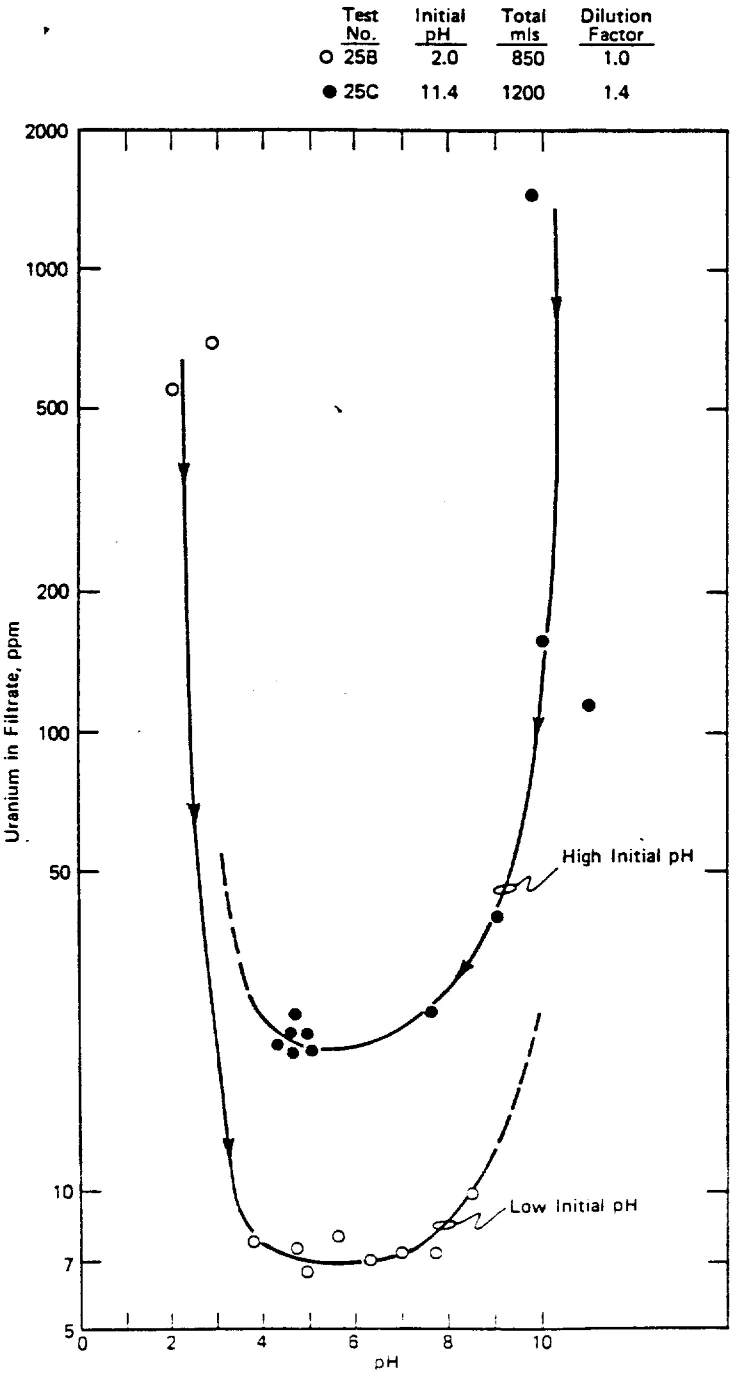

FIG. 3. Uranium in Filtrate (ppm) vs. Acid/Caustic Mixing Sequence. Caustic Recovery Solution Containing Dissolved Aluminum Used to Neutralize the Acidic Solution. The PO_4^{-3}:U Molar Ratio was 4.9.

maximized the recovery of uranium, but also significantly reduced the amounts of nickel and aluminum released to the waste treatment facilities. The removal of the key materials, under optimum conditions, is summarized below:

	Concentration, g/L		
Material	Initial	Filtrate	% Removal
U	15.1	0.007	99.95
Al	13.5	<0.001	99.99
Ni	0.7	0.002	99.71
PO_4	29.1	<0.001	99.99

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