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OVERCONCENTRATION IN INITIAL OPERATION OF
URANIUM EVAPORATOR - 321 BUILDING

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OVERCONCENTRATION IN INITIAL OPERATION OF
URANIUM EVAPORATORS - 321 BUILDING

INTRODUCTION

The Purex prototype pulse column testing facility was built, as an addition to 321 Building, to obtain confirmation of pulse column designs for the projected Purex separation plant by extended-period experimental operation of certain critical pulse columns (HA, HC, and 2A) on the full scale. The prototype test facility is designed for a nominal instantaneous uranium processing rate of 10 tons/day. The HA Column is 33 ft. in over-all height, with a 24-in. extraction-section and 32-in. scrub-section diameter. The HC Column is 23 ft. high, with a 27-in.-diameter plate section.

In conjunction with the Purex prototype HA and HC pulse column testing facility, a long-tube evaporator⁽¹⁾ has been provided for the concentration of uranium solutions for reuse in the column tests. The first process testing of this concentrator with uranium-bearing solutions took place on July 1. In the course of this initial testing, accidental overconcentration resulted in the evolution of nitrogen dioxide fumes from the concentrator. The purpose of this memorandum is to outline the facts surrounding this incident and to indicate its nature and probable causes.

SUMMARY AND CONCLUSIONS

In the initial uranium solution testing of the Purex prototype facility uranium evaporator, failure of the concentrator feed pump, along with other contributing circumstances discussed later, resulted in an overconcentration of the uranyl nitrate solution to the point of incipient denitration. The overconcentration was accompanied by the evolution of brown nitrogen dioxide fumes from the concentrator. Examination of the evaporator contents after the incident has led to the conclusion that a rapid reaction of nitric acid with organic material may also have occurred. The pressure buildup surmised to have accompanied the nitric acid-organic reaction apparently jarred the ceramic Raschig-ring packing in the stripping tower surmounting the concentrator tubes sufficiently to chip many of them badly. Ceramic dust and chips from the Raschig rings were found mixed with the uranium-bearing concentrator residue in almost the entire concentrator pot and filling more than half of the tubes.

DISCUSSION

Equipment Description

The Purex prototype pulse column testing facility uranium concentrator (sketched in Figure 1) is a modified Kestner-type vertical long-tube evaporator. Its 3-foot diameter steel steam shell envelops 640 ten-foot-long 1-inch o.d., 0.718 inch i.d. stainless-steel process tubes. The concentrator proper is surmounted by a stripping and de-entrainment tower. This tower is 6-ft. in diameter. It consists of (a) an 18-ft.-high packed section, packed with 2-in. ceramic Raschig rings, for removal of dissolved and entrained organic phase from the feed stream by steam stripping (below the

feed point); and (b) a 3-ft. high packed section above the feed point for de-entrainment. The latter is packed with 1-in. ceramic Raschig rings. The steam rising from the process solution is condensed by a jet condenser., which is vented to the atmosphere.

The concentrator is fed directly from the HC Column by means of the HCP (HC Column aqueous effluent) pump, a Durco centrifugal pump. At steady-state operation the steam flow rate to the concentrator steam chest is automatically controlled by the specific gravity of the concentrate. During startup operation, as at the time just prior to the overconcentration incident, the steam flow to the chest is controlled manually on the basis of concentrate specific gravity and liquid-level readings.

The steam supply line is under 100 lb./sq.in. gage pressure.

Uranium-Free Testing

Before the uranium solution concentration test discussed here, the evaporator was tested with (a) water and (b) water saturated with solvent (30 vol.% TBP in Shell Deodorized Spray Base). In the solvent-saturated water testing the concentrator feed was the aqueous effluent stream from the HC Column during water-versus-solvent HA and HC Column shakedown tests.

Overconcentration in First Uranium Test

The initial testing of the concentrator with uranium solution was carried out as part of a complete solvent-extraction-and-concentration cycle, involving uranium-solution shakedown testing of the HA and HC pulse columns, as well as of the concentrator. The sequence of events was as follows:

1. The pulse columns were placed in operation with only uranium-free aqueous and solvent streams flowing, and the concentrator was placed in boil-up operation with HC Column aqueous effluent (HCP), initially about 0.1 M HNO_3 , as the feed.
2. At approximately 9:00 a.m., about 90 minutes before the overconcentration occurred, the uranium-bearing pulse column feed (HAF) stream was started. This resulted in a gradually increasing uranium content in the HCP stream that was being fed to the concentrator. It is estimated that by 10:30 a.m., just before the nitrogen dioxide fume evolution, the HCP uranium concentration had closely approached the steady-state concentration of 0.2 M. The HCP nitric acid concentration is estimated at 0.12 M.
3. During the 90-minute transient-state operation which followed the start of the HAF stream the stream flow rate to the concentrator was controlled manually. Manual control was to be continued until the concentrate specific gravity, initially between 1.0 and 1.1, rose to the desired value of 1.6, and steady operation was well established. The HCP feed rate to the concentrator was determined

on the average by the HCX (HC Column aqueous influent) stream rate. Instantaneous fluctuations in the HCP flow rate resulted from the use of the HCP flow control (Hammel-Dahl) valve as the controlled element of the HC Column interface controller. The sensitivity adjustment of the controller was such that the HCP flow was almost completely shut off when the HC Column interface was too low. At such times the HCP pump overheated, necessitating shutdown of that pump for about 2 to 5 minutes three times during the 90 minutes preceding the overconcentration.

4. During the third HCP pump shutdown the uranium concentration in the concentrate must have risen above that corresponding to molten uranyl nitrate hexahydrate (UNH), with incipient denitration occurring. The concentrate specific gravity recorder, however, indicated a specific gravity of only 1.6, corresponding to less than 60% UNH solution. This falsely low indication was due to the top dip tube of the bubbler-type specific-gravity instrument no longer being submerged in liquid.
5. Emission of brown fumes, visually identified as nitrogen dioxide, from the top of the concentrator took place during the third HCP pump shutdown. The NO_2 fumes issued from the condenser vent. A hissing noise was reported heard in the first minute or so of the emission. Two engineers near the concentrator reported smelling butyric acid.
6. When the NO_2 evolution was observed all test equipment in operation was immediately shut down, and the Purex prototype facility and the adjacent buildings were evacuated as a precautionary measure. There were no personnel injuries. The fume evolution gradually subsided, in about 5 to 10 minutes.

Residue in Concentrator

After the overconcentration, much of the concentrator was filled with a heterogeneous mass containing the following:

1. Concentrated uranyl nitrate solution. (The water in this solution may have largely originated from dilution water added after the overconcentration.)
2. Uranyl nitrate crystals (degree of hydration not determined).
3. Other uranium compounds, tentatively identified as mostly UO_3 and probably some uranyl phosphate (the later being formed with phosphate ion resulting from TBP decomposition).
4. "Red oil" - an organic phase of 1.2 to 1.6 specific gravity, tentatively identified as a mixture containing uranyl nitrate - tributyl phosphate complex, uranyl nitrate - dibutyl phosphate complex, and uncomplexed TBP and DBP, as well as other organic

materials. An infrared spectrogram⁽⁴⁾ indicated this material to be similar to the "red oil" used by Wagner⁽³⁾ in his studies of "red oil" - nitric acid reactions.

5. Ceramic dust and chips, up to about 1/2 inch in size. Some of the ceramic was beige, the color of the outside of the ceramic (unglazed stoneward) Raschig rings, and some of its dark grey, the color of the incompletely baked inside of the rings.

The uranium content of various portions of this mass, between 20 and 30% for the most part, but ranging from 8 to about 72%, indicated approximately 600 lb. U in the concentrator residue. The components of the residue were mixed in a mass of putty-like consistency. The "red oil" content is roughly estimated at 3 to 10 gallons.

This residue filled almost the entire concentrator pot and completely filled about half the tubes. The tubes and pot areas nearest the recirculation downcomer pipe were freest of residue.

Inspection of Ceramic Raschig Rings

The 2-in. unglazed stoneward Raschig rings (supplied by U.S. Stoneware) in the stripping tower surmounting the concentrator were found settled to about 18 in. below their original level (out of a packed height of 18 ft.). A number of rings were found lying on top of the feed distributor, above the original level of the rings. The distributor showed signs of having been battered by ceramic rings being knocked against it. All the rings were more or less badly chipped. About 20% had broken blisters. About 20% were broken. (This, however, may not be significantly more than the percentage found broken at the time of packing.) The rings near the top and near the bottom of the packed section were chipped more severely than those in the middle regions. Some rings (predominately near the bottom) were splashed with a brownish-red material, resembling the "red oil".

Cause of Pressure Buildup

Examination of the concentrator residue and of the ceramic Raschig rings indicated that there must have been a pressure buildup in the concentrator. This pressure buildup was insufficient to rupture or distort any of the metal parts, but was sufficient to lift and jar the ceramic rings.

The pressure buildup may have been the effect of a rapid chemical reaction between a constituent of "red oil" and nitric acid. DuPont⁽²⁾ and General Electric (Hanford)⁽³⁾ workers found that such a reaction could occur at and near incipient calcination temperatures (135 to 160°C.), which were likely to have prevailed in the concentrator at the time of the incident.

Precautionary Measures - 321 Building

On the basis of the experience gained in the initial operation of the Purex prototype column testing facility uranium concentrator, the following modifications of the concentrator and its instrumentation are being made:

1. Additional nozzles are being put on the concentrator, as sketched in Figure 2, (a) to facilitate periodic clean-out, (b) to allow sampling of the concentrator liquids, and (c) to permit addition of dilution water in case of serious over-concentration.
2. The 2-in. unglazed stoneware ceramic Raschig rings in the stripping tower, which were broken and chipped, are being replaced with 2-in. unglazed porcelain rings. (Both supplied by U.S. Stoneware).
3. Automatic instrumentation designed to prevent serious over-concentration is being installed as indicated on Figure 3. Concentration control will continue to be normally accomplished by the specific gravity of the concentrate controlling the steam supply rate. New safeguards against over-concentration and the attainment of temperatures (in excess of 135°C.) at which a "red oil"-nitric acid reaction could occur, are as follows:
 - (a) An alarm bell rings if the boiling liquid temperature exceeds a selected set point (e.g. 120°C.).
 - (b) Automatic shut-off of the steam supply is accomplished if:
 - (i) The boiling temperature exceeds a selected set point (e.g. 135°C.).
 - (ii) The steam pressure in the steam chest exceeds a selected value (e.g. 40 lb./sq.in.ga.).
 - (iii) The weight factor of the concentrate falls low enough to uncover the instrument dip leg for specific gravity.
 - (c) Addition of cold dilution water to the concentrator:
 - (i) Automatically if the liquid temperature exceeds the steam-shut-off set point (e.g. 135°C. as under (b), above.
 - (ii) Manually as desired for startup or to relieve abnormal conditions.
 - (d) An indicator light and alarm bell to warn the operator if the concentrator feed pump is shut off.
4. In addition to the above-mentioned safeguards, the HC Column (bottom) interface controller is being revised and adjusted with a view to minimizing the likelihood of organic-phase entry into the concentrator.

Precautionary Measures - U. R. Plant

In the Uranium Recovery Plant safe operating conditions for the uranium concentrators are provided as follows:

1. The initial (6 to 60% UNE) concentrators receive feed from a storage tank, in which phase separation is allowed to take place, rather than directly from a pulse column. The degree of concentration is controlled by steam pressure in the concentrator chest (rather than by steam supply rate), set on the basis of overhead liquid temperature readings. This chest steam pressure is normally between 20 and 30 lb./sq.in.ga., preventing the attainment of tube temperatures in excess of about 135°C.
2. The final (60 to 100% UNE) concentrator receives from another storage tank, in which any organic phase that may have passed through an initial concentrator is allowed to separate out.

In connection with the contemplated modification of the Uranium Recovery Plant for two-cycle operation to permit processing younger wastes, the mode of operation of the inter-cycle uranium concentrator will be reviewed with a view to assuring a safe operating procedure with the proposed flow scheme.

Precautionary Measures - Purex Plant

The present preliminary design of the projected Purex Plant uranium concentrators embodies precautionary features based on the Savannah River pilot-plant experience and laboratory data. The design is receiving further attention, with the objective of incorporating such additional safeguards as may appear warranted.

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- (2) DP-25, "TNX Evaporator Incident, January 12, 1953". J. T. Colven. Jr., G. M. Nichols, and T. M. Siddall, May 15, 1953. (DuPont).
- (3) HW-27492, "Investigation of Explosive Characteristics of Purex Solvent Decomposition Products (Red Oil)". R. M. Wagner, March 17, 1953.
- (4) R. H. Moore, Applied Research Sub-Section, H.A.P.O., informal communication, July 3, 1953.

FIGURE 1
PUREX PROTOTYPE URANIUM ELAPORATOR

Figure 2

MODIFICATIONS TO PUREX PROTOTYPE URANIUM EVAPORATOR

Note: Modifications
shown in red

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Figure 3

PUREX PROCESSING CONCENTRATOR -- DECONTAMINATION SECTION