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September 30, 1954

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BIPOLAR PLANT NICKEL FERROCYANIDE SCAVENGING FLOWSHEET FOR
FIRST-CYCLE WASTE CONTAINING NO COATING-REMOVAL WASTE

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BIPO₄ PLANT NICKEL FERROCYANIDE SCAVENGING FLOWSHEET FOR
FIRST-CYCLE WASTE CONTAINING NO COATING-REMOVAL WASTE

INTRODUCTION

Additional laboratory-scale studies of the decontamination of current first-cycle waste samples from the BiPO₄ Plant using nickel ferrocyanide scavenging have confirmed earlier data obtained on synthetic and aged first-cycle wastes. (1) These recent studies indicate that the cesium and strontium in first-cycle waste is reduced by scavenging to well below the 0.1 μ c/cc. recommended by the Radiological Sciences Department for large-scale waste cribbing (6000 or more gallons/sq.ft. of crib area). (2) Scavenging of first-cycle waste resulted in a sludge volume of approximately 20%. The sludge volume obtained when scavenging a mixture of first-cycle waste and coating-removal waste was approximately 45% due to aluminum hydroxide precipitation. This excessive sludge volume along with the possible detrimental effect upon dissolver operating efficiency of tying the dissolver cycle to the waste scavenging cycle has indicated the need for segregation of the coating-removal waste. In this document a chemical flowsheet is presented for use as a design basis for facilities which will permit scavenging of first-cycle waste without coating-removal waste when the plant is processing 190-215 MWD/T uranium.

DISCUSSION

Waste Volume

The first-cycle waste volumes given on Figure 1 are based on actual plant averages obtained when processing plutonium from extraction batches containing 1.55 tons of 200-215 MWD/T uranium. (3)

Figure 1 lists two flows for each process step. The smaller flows in each case are a summation of: (1) the average first-cycle waste and sodium hydroxide volumes, (2) a 3% jet dilution whenever jet transfer occurs, and (3) the scavenger reagent volumes. The larger flows indicate the volumes actually expected during plant operation and are calculated from actual operating volumes obtained during the last three months. The larger flows should be used in the design of facilities for handling the supernate or sludge since they reflect actual operating experience. Factors which contribute to the larger flows have been enumerated on Figure 1.

Chemical and fission-product concentrations are based on the smaller flows. The nickel and ferrocyanide concentrations are also based on the smaller volumes since the addition of small amounts of miscellaneous waste is not expected to lower the scavenger concentration in the final volume to a point where additional nickel sulfate or potassium ferrocyanide would be required.

Effect of MWD/T Level

The flowsheet defines conditions for scavenging first-cycle waste produced when processing 190 to 215 MWD/T uranium in the BiPO₄ Plants. At the present time approximately 1.55 tons of 200 to 215 MWD/T uranium (approximately 300 g. Pu) are being processed per extraction batch. Should 190 MWD/T uranium be processed, a maximum batch size of approximately 1.65 tons of uranium (approximately 292 g. Pu) would be processed per extraction batch since the precipitator tank volume becomes limiting at 1.65 tons. The extremely small increase in extraction batch size along with an almost constant plutonium batch size in the first decontamination cycle will give practically constant first-cycle waste volumes when processing 190 to 215 MWD/T uranium.

Segregation of Coating-Removal Waste

Complete segregation (including separate storage) of the coating waste when scavenging first-cycle waste is desirable if maximum waste volume reduction is to be realized. For example, recent laboratory-scale studies have shown that the addition of coating waste to the first-cycle waste either before or after scavenging results in sludge volumes of approximately 45% and 30%, respectively, as compared to approximately 20% for first-cycle waste scavenged alone.⁽¹⁾ Both volume increases are due to aluminum hydroxide precipitation. If coating-removal waste and first-cycle waste are segregated and each is handled separately (i.e., first-cycle waste is scavenged and coating-removal waste is routed directly to separate storage), the total volume of waste to be permanently stored is approximately 10% less than the volume required if coating and first-cycle wastes are combined prior to neutralization and scavenging. Laboratory studies are currently being made on methods of treating coating waste to reduce further storage requirements.

By segregating and separately treating coating-removal and first-cycle waste, a slight improvement in operating efficiency of the plant may be achieved. Coating-removal waste can be sent directly to storage instead of remaining in the dissolver until it can be properly combined with scavenged first-cycle waste in the neutralizer.

Sludge Heating

Calculations have been made to determine the amount of heat which will be evolved in the tanks containing the sludge from the scavenging operation. It is concluded that a tank full of sludge may be stored without boiling for average processing rates in one BiPO₄ Plant as high as 5 ton/day (150 tons/month). The uranium was assumed to have been subjected to an integrated pile exposure of 105 MWD/T and a pile power level of 5.6 megawatts/ton.

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In arriving at the above conclusions regarding sludge heating, certain safe-side assumptions were made, as follows:

1. It was assumed that a fission-product D.F. of 5 was obtained on the plutonium across the extraction cycle and that all the fission products present in the extraction cake solution would be carried out in the first-cycle waste.
2. It was assumed that all the fission products present in the first-cycle waste would be precipitated with the ferrocyanide slurry. Actually, roughly 1% of the fission products will be discharged to cribs in the supernate.
3. It was assumed that the slurry would settle to a final sludge storage volume of approximately 200 gal./ton of uranium processed. This settled volume is approximately 50% of the sludge volume shown on Figure 1. Although the flowsheet volume is believed to be realistic, the smaller volume was used in the heating calculation to allow for possible compacting in the tank.
4. It was assumed that a 550,000 gallon waste storage tank would be operated continuously until filled with sludge (i.e., 1000 gal. of sludge was added to the tank each day). In actual plant practice, presumably operations will be switched from one tank to another. After a tank has been filled with scavenged waste, a second tank is filled while the first tank settles and the supernatant liquid is decanted to cribs. With this method of tank scheduling, the rate of sludge (and fission product) addition to the tank would be slower than that assumed in the calculations.
5. It was assumed that heat losses to the ground from the 550,000 gal. tank would be approximately 400,000 Btu/hr. at the period of peak heat evolution.

Sludge Settling Characteristics

Preliminary laboratory studies on the sludge settling rate have indicated the presence of a finely divided solid which settles slowly. This fine material settles at the rate of approximately 1 ft./day as compared to 1 ft./hr. for the heavy solids. In order to insure complete settling, a minimum settling time of three weeks should be employed on each tank prior to supernate decanting and cribbing.

Additional studies are currently being made in the laboratory in an attempt to reduce the settling time requirements.

REFERENCES

- (1) HW-32716 "Decontamination of Bismuth Phosphate Process First-Cycle and Coating-Removal Wastes." R. E. Burns, August 10, 1954.
- (2) HW-30652 "TEP Waste Disposal Project Criteria for Cribbing Scavenged RAW." H. V. Clukey, January 27, 1954.
- (3) W. C. Schmidt, Separations Technology Sub-Section, H.A.P.O., informal communication, September 22, 1954.

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FIGURE 1

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NICKEL FERROCYANIDE SCAVENGING OF FIRST-CYCLE BIPO₄ WASTE WHICH CONTAINS NO COATING-REMOVAL WASTE

(Flowsheet for scavenging First-Cycle Waste Produced from 190 - 215 MWD/T Uranium Processing in the BIPO₄ Plant)

NOTES:

- Flows are based on actual plant averages per batch when processing 200 - 215 MWD/T uranium in batches of 300 g. Fe (1.55 ton U/batch for 200 - 215 MWD/T uranium or 1.65 ton U/batch for 190 MWD/T uranium).
- The flows listed from the waste neutraliser to U.G.S. are given as a range. The smaller flow is based on the summation of entering flows plus a 10% jet dilution allowance for each jet transfer. The larger flows are calculated from actual plant averages. In the case of the neutralized waste volumes the difference may be explained by one or more of the following: (a) a jet dilution of greater than 1%, (b) addition of unmeasured amounts of stack-drainage waste. In the case of the settling tanks, the difference may be explained by one or more of the following: (a) a jet dilution of greater than 1%, (b) addition of neutralized waste from acid flushes, or (c) addition of diversion box flush water. All concentrations are based on the smaller flow.
- Sludge volume is 20% of scavenged, neutralized waste volume.
- Potassium ferrocyanide and nickel sulfate additions should be varied with the volume of waste produced. Sufficient potassium ferrocyanide and nickel sulfate should be added to produce approximately 0.005 M ferrocyanide and nickel concentrations in the neutralized waste.
- Essentially all of the ferrocyanide will be present in the sludge. The anions associated with the ferrocyanide are not positively known. Cesium and iron complexes are believed to be formed.
- Fission-product concentrations (countable curies) are based on the analyses given in HW-32716 which are based on beta-counting at 7.5% geometry and gamma counting at 3.34% geometry (Ca¹³⁷) using clear solutions only. Solids in the samples were centrifuged out.
- Settling rate data have not been obtained in deep vessels. Small-scale lab studies indicate, however, that settling rates approach 0.5 in./hr.

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