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January 1, 1954

TRANSMITTAL CONTROL NUMBER

HANFORD

54133

TO: C. A. Rohrmann
FROM: R. J. Sloat

TBP PLANT NICKEL FERROCYANIDE SCAVENGING FLOWSHEET

MASTER

INTRODUCTION

Recent plant-scale scavenging and cribbing tests have confirmed laboratory data which indicated that the cesium and strontium in TBP wastes could be reduced by nickel ferrocyanide scavenging to concentrations which permit discharge of the scavenged supernatant to cribs. In this document a chemical flowsheet is presented for use as a design basis for facilities which will permit scavenging of unconcentrated neutralized waste for the TBP Plant. /end

DISCUSSION

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Waste Volume. The combined waste volume shown on the attached flowsheet has been calculated from the HW No. 6 TBP Flowsheet. It represents the waste volume which might be expected if flowsheet feeds were consistently

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processed in the plant. Since the TBP Plant feed composition varies considerably from batch to batch the volume of waste produced from the plant has been greater than the flowsheet value. Past plant experience indicates that cribs and sludge storage facilities should be sized to handle volumes as much as 20% greater than the volumes shown on Figure 1. If the facilities for waste scavenging are available by April, 1954, approximately 3000 tons of uranium will remain to be processed in the TBP Plant. Consequently, 25 to 35 million gallons of neutralized-scavenged waste will be discharged from the TBP Plant to the settling tanks. The bulk of this waste will be discharged to cribs. Approximately 2.5 to 3 million gallons of sludge would be permanently stored.

Storage of Scavenged Waste. As is indicated on Figure 1, the sludge from the scavenged waste contains at least half of the uranium* and essentially all of the Sr and Cs originally present in the TBP wastes. Since it may be desirable in the future to recover the uranium and/or the Cs and Sr from the sludge (preliminary laboratory feasibility studies are currently in progress), the tankage presently equipped with sludge removal facilities should be used for the scavenged wastes. In addition, the number of cascades used for storage should be kept low, so that any future removal operations would be confined to a few cascades.

Fission Product Concentrations. Although the major portion of the uranium remaining to be processed through the TBP Plant is aged greater than one year, this figure has been chosen as the calculation basis for the flowsheet. In calculating the fission product concentrations it was assumed that the uranium was subjected to an integrated pile exposure of 600 MWD/ton and that the pile power level was 2.2 Megawatts/ton.

Laboratory data have not been obtained which permit prediction of the relative amounts of short-lived fission products in the supernate and sludge. Although the concentrations of the short-half-life fission products in the supernate are unimportant from a cribbing standpoint (these fission products decay to a tolerable level before reaching the water table.), they are important in designing the shielding (surface or buried lines) for the lines leading to the cribs. For the 1-year-aged waste of the flowsheet, the gross gamma concentration of the supernate could be as high as 2 curies/gal. with Ru^{106} , Zr^{95} , and Nb^{95} all contributing approximately the same amount to the total.

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. From the calculations it is concluded that a tank full of sludge may be stored without boiling as long as the minimum age of the waste (time since pile discharge) is two years. When the age of the scavenged waste decreases below two years, the sludge should not be

*) At pH 8.5 to 9 the supernate from waste scavenging contains approximately 0.15 g.U/l. With a 1% Plant loss, it is estimated that half the uranium will be precipitated with the sludge. At higher TBP Plant uranium waste losses a greater portion of the uranium originally present in the combined waste will be precipitated in the sludge.

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allowed to accumulate in the first tank of a cascade. Instead, the sludge and supernate should be discharged together into storage tanks where settling may occur. When the waste has "cooled" sufficiently, the supernatant may be decanted and the tanks refilled with other wastes. The amount of waste to be stored in this manner will be relatively small. If an average Bismuth Phosphate processing rate of 15 tons/month is assumed from July 1, 1953, until July 1, 1955, the waste resulting from processing approximately 360 tons of uranium through the TBP Plant must be temporarily stored. If this waste were stored as neutralized, unconcentrated scavenged waste, approximately 3 million gallons of storage space would be temporarily required. Only approximately 300,000 gallons of this space would be eventually required for permanent storage of the iron hydroxide and nickel ferrocyanide sludge after decanting and cribbing the supernate.

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

1. It was assumed that all the fission products present in the TBP waste would be precipitated with the ferrocyanide slurry. Actually, a good portion (probably greater than 50%) of the short-lived fission products will be discharged to cribs in the supernatant.
2. It was assumed that the slurry would settle to a final sludge storage volume of approximately 300 gal./ton of uranium processed through the TBP Plant. This settled volume is approximately 40% of the sludge volume shown on Figure 1. Although the flowsheet volume is believed to be realistic, the smaller volume was used in sludge heating calculations to allow for compacting in the tank and to permit later flowsheet changes which may reduce the sludge volume (e.g., substitution of oxalate for iron in the RA Column.)
3. It was assumed that a 550,000 gallon waste storage tank would be filled with sludge greater than two years old. It was assumed the sludge will be produced from the available wastes aged as close to 2 years as possible. In actual plant practice, presumably wastes will be alternated from one cascade to another. Consequently, wastes aged approximately two years would be mixed with older sludges.
4. 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.

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Scavenging of Previously Stored TBP Waste. The above discussion applies to the scavenging of wastes to be produced by the TBP Plant after the required plant modifications are completed in March or April, 1954. As storage volume is made available by scavenging current TBP wastes, the way will be opened for scavenging of the approximately 18 million gallons of unscavenged neutralized concentrated waste already produced from TBP processing of 3,300 tons of uranium. (Of this 18 million gallons, approximately 8 million gallons will have been concentrated to approximately 5 million gallons in the 1st cycle waste evaporation). A tentative method to be used

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for scavenging of these wastes involving the use of the TBP tank farm mining and waste acidification facilities was presented in HW-28715, Copper Ferrocyanide Scavenging of TBP Wastes. Since uranium removal operations will soon be completed in "C" and "U" Farms, dissolution facilities in these farms could be used for treatment of the unscavenged wastes.

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NICKEL FERRO

NOTES:

- (1) Although the age of most of the TBP Plant wastes will be at least two years, it is possible that some of the waste is year aged waste produced from 600 MW/ton uranium (2.2 megawatts/ton - 250 day pile exposure).
- (2) The proportion of the short half-life fission products remaining in the sludge has not been determined. In the flowsheet above, it has been assumed that all the short-lived fission products are in the waste storage tanks.
- (3) The sludge volume shown above is conservative (i.e., greater than the volume which will be required for storage). Modifications (e.g., substitution of oxalate for ferrous ammonium sulfate and sulfamic acid for ferrous sulfate) may be made. If these modifications are made, the volume of sludge stored may be decreased to approx. 300 gal./ton of U processed.
- (4) Essentially all of the ferrocyanide will be present in the sludge. The anions associated with the ferrocyanide will be present in the supernate.
- (5) Potassium ferrocyanide and nickel sulfate additions should be varied with the volume of waste processed. A concentration of 0.005 M ferrocyanide and nickel concentrations in the composite scavenged waste sent to the sludge tanks should be maintained.
- (6) If the TBP Plant uranium waste loss is 1% of the U processed, approximately half of this loss will be in the supernate. A supernate uranium concentration is not expected to increase. Consequently, a greater percentage of the uranium will be in the sludge. If the supernate uranium concentration is not expected to increase, a greater percentage of the uranium will be in the sludge.

Figure 1

CYANIDE SCAVENGING OF TRP PLANT WASTE

that waste aged less than one year may be processed. | Fission product concentrations are based on a 1
 (assumed). *Delete*

is determined. Presumably a relatively large portion of the ruthenium, zirconium, and niobium will be
 fission products end up in the sludge, resulting in a conservative calculation of heating effects in

stored) and is quoted to permit calculation of the maximum sludge storage capacity. With flowsheet
 in the RA Column, and/or reduction of scavenger concentrations) and packing of sludge in the storage
 This smaller volume has been used in estimating maximum heating effects in the sludge layer.

with the ferrocyanide are not positively known. Cesium and iron complexes are believed to be formed.

ate produced. Sufficient potassium ferrocyanide and nickel sulfate should be added to produce
 settling tanks.

uranium is found in the stored sludges as indicated above. At higher plant uranium waste losses the
 loss of the uranium present in the Plant Waste is found in the stored sludges as Plant uranium losses

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