L. W. Finch
Process Engineer
Process Sub-Section
Separations Section

TEST PROCEDURE TO EVALUATE SCAVENGING OF TBP PLANT
SOLVENT EXTRACTION WASTE WITH NICKEL FERROCYANIDE

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The TBP Plant, over the life of the operation, will be required to attain maximum recovery of stored uranium and to produce aqueous wastes in a volume equivalent to the volume of the stored uranium waste which, after acidification, constitutes the feed stream for the process. Due to the variations in the composition of the feed stream, the waste stream does not necessarily consistently have a volume equivalent to the stored metal waste. This variation in volume equivalence impedes tank farm scheduling because of the necessity for return of the process waste to underground tanks made available by the recovery operation.

More important to the long range HAP0 economics is the use of underground storage, with initial costs of approximately 35 to 45 cents per gallon and current replacement costs of 22 cents per gallon, for these comparatively moderate activity TBP wastes. A means of removing the long-lived fission products has been the objective of the investigations conducted by the Applied Research Sub-Section, since studies conducted by the Radiological Sciences Department indicate that long-lived Cs-137 and Sr-90 are the isotope which could migrate and enter the biological cycle via underground water movement.

A chemical operation, using copper ferrocyanide, which may satisfy the requirements, has recently been documented in HW-28408 (1). This scheme may permit cribbing of the major volume (75 to 85 per cent) of the recovery process unconcentrated waste and utilize only 20 to 40 per cent as much underground storage space as is now required.

Later data (2) obtained by the Applied Research Sub-Section indicate that the use of nickel ferrocyanide will give decontamination factors equivalent to the copper ferrocyanide but does not require the same high degree of pH control. In HW-28434 (3) the Separations Processes Committee recommended that chemicals be ordered for a plant test of approximately 500,000 gallons of waste.

OBJECTIVE

This memorandum has been prepared to define the proposed plant waste scavenging test and to present an operating flow diagram and operating procedures for use during the test.

SUMMARY AND CONCLUSION

Removal of cesium and strontium from Metal Recovery Plant wastes by scavenging on a precipitate of nickel ferrocyanide (Ni₂Fe(CN)₆·xH₂O) has been demonstrated on a laboratory scale to achieve a 3000 and 35-fold reduction of cesium and strontium, respectively. (2). The residual activity in the liquid phase is approximately 10 and 1000 fold above drinking water tolerances for Cs and Sr., respectively.
Investigations indicate that the principles employed may be adapted to plant equipment to attain comparable decontamination with a resultant reduction in the underground storage tank requirement of approximately 2400 to 3200 gallons per ton of uranium processed through the TBP Plant. A recommended operating procedure and a process chemical flowsheet are attached. (Appendix A and Figure I.) The successful demonstration and adoption of the scavenging process for routine plant operation will also permit the use of the existing waste concentrators (with minor jumper changes) for other process requirements (two cycle plant operation). Also, steam consumption will be reduced approximately 16,000 pounds per ton of uranium processed.

Nickel sulfate and potassium ferrocyanide costs are expected to be approximately $0.008 to $0.01 per gallon of waste treated. Labor costs are not expected to be significantly different than for the present plant operation.

If the nickel ferrocyanide fails to decontaminate the TBP Plant wastes sufficiently, so that the final settled supernatant may not be cribbed, the first cycle evaporators may be used for concentration of the waste. The first cycle evaporators have a demonstrated capacity of 300,000 gallons of TBP Plant waste per month.

DISCUSSION

The use of nickel ferrocyanide as a cesium and strontium scavenger for TBP wastes has been studied in the laboratory (2) and the effects of such process variables as reagent concentration (NISO₄ and K₄Fe(CN)₆), pH, and temperature have been examined. Upon evaluation of these process variables, the nickel ferrocyanide technique appears superior to other principal alternatives such as the cupric ferrocyanide procedure which is limited by close pH control (pH 6 to 8) or the ferric ferrocyanide procedure which is limited to a low pH range (pH 6 or less) where corrosion of mild steel is a serious limitation preventing plant application.

The nickel ferrocyanide scavenger is formed in a basic solution (pH 8 to 10) which may be stored in the underground black-iron waste tanks.

In HW-28715 (4), three different chemical procedures for use of cupric ferrocyanide as a scavenger for TBP Plant wastes were described. The method presented below, using nickel ferrocyanide as a scavenger, is similar to Method 2.

TREATMENT OF RAW

The acidic RAW is buttressed with K₄Fe(CN)₆ · 3H₂O to 0.005 M; next, the solution is neutralized with NaOH to a pH of 9 to 10; and then, the scavenger
is formed by making the neutralized solution 0.005 M in Ni\(^{2+}\) ion by adding NiSO\(_4\). The solution is then agitated and pumped to the underground tanks for storage (101-T for the test). Close pH control is not necessary but going below 8 or above 10 tends to decrease the net scavenging decontamination obtained. Further laboratory studies, with a time cycle equivalent to the plant time cycle, indicate that the plant DF obtained should be equivalent to the laboratory DF for Cs and Sr. A pH of greater than 10.5 may cause a hydrolysis of the nickel ferrocyanide with a resultant reduction in the cesium and strontium decontamination. It is believed that the present plant pH control is satisfactory for the operation of the scavenging test. Past plant results have given pH values of 6.5 to 10.5 while controlling in the range of 8 to 9 but the average values were approximately 8.4.

Method of Addition

Laboratory studies indicate that the addition of the potassium ferrocyanide to the acidic solution prior to neutralization, with the addition of nickel sulfate after, does not hinder the formation of nickel ferrocyanide or the decontamination of cesium or strontium. The reverse method of addition (i.e. add NiSO\(_4\), neutralize, add K\(_4\)Fe(CN)\(_6\)) appears to at least delay the formation of nickel ferrocyanide and may also give a lower cesium and strontium decontamination.

Temperature

Temperature appears to have little effect upon the final decontamination obtained. Heating, in the laboratory, of the acidic solution containing potassium ferrocyanide produced a gas having the odor of bitter almonds (possibly HCN). Further investigation of this gas formation gave no positive indication of the release of cyanide under conditions more vigorous than would be expected in the plant concentrators if they were operated. In the plant, the acid solution containing the potassium ferrocyanide is not heated and should not present a problem.

Equipment

In the TBP Plant, it is planned to carry out the scavenging test with very little modification to plant equipment. Later modification may be necessary pending successful completion of the test. The only change necessary for the test is the installation of an air sparger on four scale tanks for agitation during chemical makeup of K\(_4\)Fe(CN)\(_6\) \(\cdot\) 3H\(_2\)O and NiSO\(_4\) \(\cdot\) 6H\(_2\)O. The list of tanks to be used with modifications to be made is given below:
Nickel Ferrocyanide Properties

Preliminary laboratory studies indicate that the nickel ferrocyanide precipitate settles completely in approximately five days leaving a clear supernatant liquid (60 to 80 per cent clear). The precipitate is somewhat similar in physical properties to the ferric hydroxide precipitate formed during the present normal waste neutralization. The pumps or jets should be able to handle the precipitate with no difficulty and without damage to the pump bearings. Although quantitative measurements have not been made, qualitative observations indicate that the precipitate volume of the nickel ferrocyanide is approximately the same as that of the ferric hydroxide precipitate formed during normal waste neutralization.

Economic Considerations

For every gallon of concentrated waste currently sent to storage, approximately 0.6 to 0.8 gallon would be made available for storage of other "hot" waste if nickel ferrocyanide scavenging produces a cribbable supernatant. From a 500,000 gallon tank of scavenged, unconcentrated TBP waste, approximately 390,000 to 445,000 gallons of waste worth $85,000 to $96,000 (based on the $0.22/gal. cost estimate for SX Farm) would be made available.

If the 500,000 gallons of unconcentrated waste (produced from approximately 65 tons of uranium) were sent to the first-cycle waste evaporators instead of the scavenging treatment, approximately 330,000 gallons of storage space worth $73,000 would be made available. Comparing the first-cycle waste evaporation with the nickel ferrocyanide scavenging technique, it is found that 60,000 to 115,000 gallons more storage space worth from $12,000 to $25,000 is made available by employing the scavenging technique.

From this $12,000 to $25,000 must be subtracted the cribbing and chemical costs. Chemicals for the scavenging treatment of 500,000 gallons (based on NiSO₄·6H₂O and K₄Fe(CN)$_6·3$H₂O costs of $0.36 and $0.23/lb. respectively) cost approximately $4,000. This leaves $8,000 to $21,000 for the construction of cribs capable of handling 400,000 gallons or more.
Neither the cost of operating the first cycle evaporators nor the steam savings realized by not concentrating in the TBP Plant have been included in the above cost figures.

By

M. J. Stedwell

Leader, T & U Plant Process Technology
Plant Processes Unit
Separations Technology Sub-Section
Technical Section

J. G. Bradley/MJS/efg

References:


(2) Informal communication: R. E. Burns to M. J. Stedwell.

(3) HW-28434, "Separations Process Committee Minutes", O. F. Beaulieu.

(4) HW-28715, "Copper Ferrocyanide Scavenging of TBP Wastes", R. J. Sloat.


(6) Informal communication: N. G. Wittenbrock to M. J. Stedwell.
FIGURE I

NICKEL FERROCYANIDE WASTE SCAVENGING CHEMICAL FLOWSHEET

Tk-X-11
K₄Fe(CN)₆·3H₂O
200 Lb. 80 Gal.

Pump

Raw-Row
Pooled
Receiver
Tk-13-6
10,000 gal.

TK-X-12
K₄Fe(CN)₆·3H₂O
200 Lb. 80 gal.

TK-X-13
K₄Fe(CN)₆·3H₂O
200 Lb. 80 gal.

TK-12-1

TK-12-6

Pump

NaOH Add
13,000 Lb.
1,040 gal.

Waste
Sampler
TK-11-1
10,000 gal.

Waste
Neutralizer
TK-11-6
11,200 gal.

Pump

TK-X-09
NiSO₄·6H₂O
105 Lb. 34 gal.

Pump Via 9-1,9-2

Waste Conc.
Feed
Tk-9-6
4,800 gal.

Conc. Waste
Receiver
TK-9-7
4,800 gal.

241-WR-001
and
Subsequent
Tank Farm
Storage
(For Test, 101-T)

Via 10-1, 10-2

TK-10-6

Jet

TK-10-7

Jet Via 4-6

TK-8-6

TK-8-7

TK-13-1
OPERATING PROCEDURE FOR NICKEL FERROCYANIDE SCAVENGING

1. One hour before start of neutralization, after the sample has been taken, start the agitator on Tk. 11-1 (12-1, 12-6, 13-1).

2. Obtain supervisor's approval to add ___ pounds of potassium ferrocyanide solution to Tk. 11-1, (12-1, 12-6, 13-1) from scale tank X-11, (12, 13).

(Note to supervisor - Calculate butt assuming a heel in the waste sampler tank of 1100 gal.).

Basis of Butt = 79 lb. of 26% K₄Fe(CN)₆·3H₂O per 1000 gal. of pooled waste minus heel of pooled waste from previous batch.

3. Start neutralization per standard procedure.

4. Pump neutralized waste to the empty concentrator feed and receiver tanks 9-6, 9-7, (10-6, 10-7) without operation of concentration until the high level point is reached. Then stop transfer.

5. Start the 9-6 and 9-7 (10-6 and 10-7) agitators.

6. Obtain supervisor's approval to butt 9-6, (10-6) with ___ pounds and 9-7 (10-7) with ___ pounds of 26% NiSO₄·6H₂O via the X-09 scale tank.

(Note to Supervisor: (Butt with 35.7 lbs. of 26% NiSO₄·6H₂O per 1000 gal. neutralized solution minus solution heel remaining from previous batch in the tanks.

7. Pump 9-6 and 9-7 (10-6 and 10-7) to WR-001 before refilling from 11-6.

- Waste Batch No.
- Date
- Time On
- Scale tank
- Wt. before
- Scale Tank
- Wt. After
- Pounds add
- Time add
- Time started
- Time end
- Time start
- Time end
- -6 wt. ftr.
- -7 wt. ftr.
- Time on
- 9-6(10-6) Butt,
- X-09 start wt.
- X-09 final wt.
- Pounds add
- 9-7(10-7) Butt,
- X-09 start wt.
- X-09 final wt.
- Pounds add
- Time add
- Time 9-6(10-6) MT
- Time 9-7(10-7) MT

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END

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