F/H ETF; evaporator overheads, bottoms; mercury; ammonia
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CALCULATIONS OF VOLATILITIES OF Hg, NH_3, and Cs-137 IN THE F/H EFFLUENT TREATMENT FACILITY EVAPORATOR SYSTEM

INTRODUCTION

An evaporator will be used in the F/H Effluent Treatment Facility (F/H ETF) to reduce the volume of effluent dispensed to Upper Three Runs Creek and to concentrate solutions from three sources in the F/H ETF before sending that waste to Saltstone. The evaporator will be fed by backwash from the filters in the filtration unit, the concentrate stream from reverse osmosis, and the solutions used in regeneration of ion exchange columns.(See Figure 1.) These streams will contain small amounts of Hg, NH_3, and Cs-137. Data is readily available concerning the entrainment of these chemicals in evaporator overheads during an evaporation process. No data has yet been generated to predict their behavior due exclusively to their volatility, however. This document describes calculations that have been made concerning the volatility of Hg, NH_3, and Cs-137 compounds in the F/H ETF evaporator based on expected concentrations, temperatures, and flow rates in that facility.

SUMMARY

If all the mercury present in the stream coming into the evaporator is ionic mercury, Hg^{2+}, no mercury metal will be introduced to the overheads due to volatilization; mercury will be carried over exclusively by entrainment. If, however, Hg^{2+} is reduced by some undetermined mechanism, calculations show that all of the mercury will be volatilized to the overheads.

At an ammonium ion concentration of 0.0083 molal [1] and a feed pH of 6.5, the resulting concentration of NH_3 in the overheads at 25°C will be 6.5 E-5 molal and the pH of the overheads will be 9.4. The NH_3 concentration left in the bottoms will be 0.082 molal and the pH of the bottoms at 25°C will be 4.5. When the overhead stream is blended with the ion exchange effluent stream, assuming that stream will be at a pH of 6.5, the resulting mixture will be dispensed to the creek at 8.4 for average conditions and at 7.9 when ammonium/ ammonia concentrations in the ion exchange effluent are maximized.

No volatile compounds of cesium are expected to be formed in the evaporator at 100°C and the presence of any Cs-137 in the overheads will be due entirely to entrainment.

MERCURY

Mercury volatility and expected concentration in evaporator overheads were based on the worst-case situation wherein the solution in the evaporator is considered to be saturated with metallic mercury. At 100°C, the vapor pressure of mercury is 0.2729 torr. Using the ideal gas law for a volume of 1 liter of water evaporated, the amount of mercury volatilizing with the water will be 3.99 g Hg/liter of water.

$PV = nRT$ where $P = 0.2729/760$ atm.
$V = 55.6\ RT$ (moles/atm)
$R = 0.0821$ L atm/°K mole
$T = 373$°K

$$n = PV/RT = \frac{[0.2729/760 \text{ atm}][55.6 \text{ RT moles/atm}]}{RT} = 2.00 \text{ E-2 moles Hg}$$

$$\text{g Hg} = [2.00 \text{ E-2 moles Hg}][200 \text{ g/mole}] = 3.99 \text{ g Hg/L water}$$

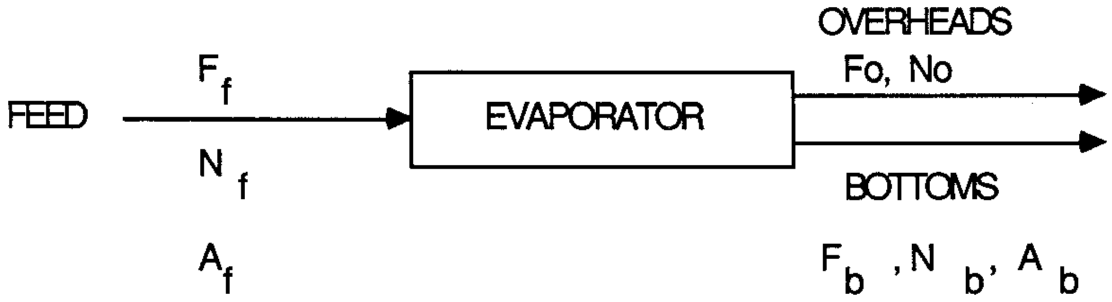
At an evaporator overhead flowrate of 18 gal/min, this computes to

$$[18 \text{ gal/min}][60 \text{ min/hr}][3.78 \text{ L/gal}][3.99 \text{ g Hg/L}][1 \text{ lb/454 g}] = 35.9 \text{ lb Hg/hr.}$$

The expected maximum influent concentration of mercury to the evaporator will be 0.64 ppm, or 6.4 E-4 g/L, as Hg^{2+}. No substance that could form volatile complexes with Hg will be present. It has not been demonstrated at this time whether there are chemical species in the stream that will reduce Hg^{2+} to metallic mercury. For example, although reduction by NH_3 is a thermodynamically feasible process, it has not yet been ascertained that reduction will proceed under the conditions in the stream. If no reduction takes place, the only mercury expected in the overheads should be there because of entrainment. But, if reduction to the metal does occur, the maximum concentration of metallic mercury in the evaporator would be 6.4 E-4 g/L. (The presence of metallic mercury has been reported during normal operation of Tank Farm evaporators.) Since this number is less than that calculated for the saturated system (3.99 g/L), all the mercury would be expected to vaporize into the overheads, generating a stream containing 5.75 E-3 lb/hr Hg as a worst case situation.

AMMONIA

To determine the distribution of ammonia, NH_3, in overheads and bottoms after evaporation as a result of volatilization only, the following scheme was derived.



Let F_f, F_o, F_b be flow rates of Feed, Overheads, and Bottoms, respectively. (Kg water/min)

N refers to molal concentration of ammonia derived species in each stream.

A is the molal concentration of a permanent, non-volatile anion which is nitrate, here.

Mass balance among streams:

$$F_f = F_o + F_b \qquad (1)$$

$$F_fA_f = F_bA_b \qquad \{A_o = 0\} \qquad (2)$$

$$F_fN_f = F_oN_o + F_bN_b \qquad (3)$$

Equilibria Considered

$$NH_3 + H^+ \rightleftharpoons NH_4^+ \qquad Ka = \frac{[NH_4^+]}{[NH_3][H^+]} \qquad (4)$$

$$H^+ + OH^- \rightleftharpoons H_2O \qquad Kw = [H^+][OH^-] \qquad (5)$$

$$NH_3(aq) \rightleftharpoons NH_3\ (g) \qquad Kp = P_{NH3}/[NH_3]\ \text{atm/(mole/kg)} \qquad (6)$$

Mass Balance for Any Given Solution

$$N = [NH_4^+] + [NH_3] \qquad (7)$$

$$N = [NH_3]\ \{1 + Ka[H^+]\} \qquad (8)$$

$$N = [NH_4^+]\ \{(1 + Ka[H^+])/\ Ka[H^+]\} \qquad (9)$$

$$[NH_4^+] = N\ Ka[H^+]/\ (1 + Ka[H^+]) \qquad (10)$$

Charge Balance

$$[H^+] + [NH_4^+] = [A^-] + [OH^-] \qquad (11)$$

(Other ions such as Na^+ and NO_3^- may be present but their concentrations will cancel.)

$$[H^+] + N\ Ka[H^+]/(1 + Ka[H^+]) = [A^-] + Kw/\ [H^+] \qquad (12)$$

To calculate the concentration of NH_3 in condensed overheads:

(a.) Calculate the volume of steam generated by 1 kg of water at 1 atm.

$$V = \frac{1000\ g\ RT}{(18\ g/mole) \times 1\ atm} = 55.6\ RT \qquad (13)$$

(b.) Calculate the number of moles of NH_3 in this volume.

$$No = (P_{NH3}V)/RT = 55.6\ P_{NH3} \qquad (14)$$

From Equation (6), $P_{NH3} = Kp[NH_3]_b$ (15)

where $[NH_3]_b$ is the free ammonia concentration in the bottoms.

Hence, $N_o = 55.6\ Kp[NH_3]_b$ (16)

or, from Equation (8),

$$N_o = 55.6\ KpN_b/(\ 1 + Ka[H^+]_b)$$

Calculations:

It is necessary to calculate the initial conditions of the solution. If the only things that are known are the initial concentration of ammonia derived species, N_f, and the pH, Equation (12) can be used to determine the concentration, A_f, of permanent anion associated with $NH_4{}^+$ and H^+.

$$A_f = [H^+]_f + N_f\ Ka[H^+]_f/(\ 1 + Ka[H^+]_f) - Kw/\ [H^+]_f$$

From Equation (2),

$$A_b = (A_f\ F_f)/F_b\ ,$$

and, from Equation (3)

$$N_f = (N_o\ F_o)/F_f + (N_b\ F_b)/F_f.$$

Let $\Phi_o = F_o/F_f$ and $\Phi_b = F_b/F_f$. Then,

$$N_f = \Phi_o N_o + \Phi_b N_b$$

But, $N_o = \beta N_b/(1 + Ka[H^+]_b)$ where $\beta = 55.6K_p$

Therefore, $N_f = N_b\{[\ \Phi_b(1 + Ka[H^+]_b) + \Phi_o\beta]/(1 + Ka[H^+]_b)\}$ and

$$N_b = N_f[(1 + Ka[H^+]_b)/\ \Phi_b(1 + Ka[H^+]_b) + \Phi_o\beta].$$

Substitution into (12) yields

$$[H^+]_b + N\ Ka[H^+]_b\ /[\Phi_b(1+Ka[H^+]_b)+\Phi_o\beta] = A_b + Kw/\ [H^+]_b.$$

Appendix 1 contains a computer program that calculates the ammonia concentration and the pH of the overheads and the bottoms of the evaporator. The results of the computation are recorded in Table 1. Two values neccessary for the computation were not readily available in the literature. Those were K_p at 100°C and Ka at 100°C. These values were calculated from existing data (See Appendices 2 and 3) at lower temperatures using standard thermodynamic techniques.

The final pH of the stream dispensed to Upper Three Runs Creek is of concern. A simple calculation using the data generated by the computer program for a maximum total ammonium/ammonia feed concentration from ion exchange at pH 6.5 shows that the combined effluent from evaporator overheads and ion exchange will have a pH of 7.9 when dispensed. For average conditions, the final pH will be 8.4. These calculations, based on flow rates in Fig. 1, are shown in Appendix 4.

CESIUM

There should be no volatile cesium compounds in the evaporator. Thus, any cesium found in the overheads will be due to entrainment.

REFERENCES

1. RYAN, J. P., and STIMSON, R. E., "Technical Data Summary, F/H Effluent Treatment Facility", DPSTD-84-114, December, 1984.

2. *Stability Constants of Metal-Ion Complexes*, The Chemical Society, Burlington House, London, 1964, Vol. 1, p. 150.

3. KIRKPATRICK, P. C.,*Perry's Chemical Engineers' Handbook,* 4th Ed., McGraw-Hill, New York, New York, p 14-4.

APPENDIX 1

A Program in Basic to Calculate pH and NH_3 Concentrations

```
REM --- THIS PROGRAM CALCULATES THE AMMONIA CONCENTRATION AND THE PH OF THE
         'OVERHEADS AND BOTTOMS OF AN EVAPORATOR , GIVEN THE FOLLOWING:
         'THE FRACTION 0F THE FEED GOING TO THE BOTTOMS, - THEB
         'THE MOLALITY OF AMMONIA-AMMONIUM IN FEED, -  NF
         'THE PH OF THE FEED, - PHF
 INPUT "FRACTION OF FEED GOING TO BOTTOMS = ", THEB
 INPUT " INITIAL NH3 -NH4  MOLALITY = " , NF
 INPUT " INITIAL PH OF FEED  = " , PHF
 REM --- EQUILIBRIUM CONSTANTS AND OTHER DEFINED PARAMETERS FOLLOW:
        'KAC AND KAH ARE ASSOCIATION CONSTANTS OF NH4 AT 25 AND 100 RESPECTIVELY
       'KWC AND KWH ARE THE DISSOCIATION CONSTANTS OF H2O AT 25 AND 100
       'RESPECTIVELY
        'KP IS THE SOLUBILITY CONSTANT OF NH3 AT 100 (ATM -KG/MOLE)
        'CMAX IS THE MAXIMUM NUMBER OF ITERATIONS IN THE PH DETERMINATIONS
    KAC =1.757E+09
    KAH = 3.573E+07
    KWC = 1E-14
    KWH = 5.508E-13
    KP = .227
    CMAX = 12
 REM --- NOW START CALCUTATIONS
    THEO = 1!-THEB
    BETA = 55.56*KP
    LTEN = LOG(10)
 REM --- NOW CALCULATE ANION CONC. OF FEED AF, FROM PH MEASURED AT 25
    HF = EXP (-LTEN*PHF)
    X = KAC*HF
    AF = HF + NF*X/(1!+X) - KWC/HF
 REM --- NOW CALCULATE ANION CONC. AB IN BOTTOMS
    AB = AF/THEB
 REM --- NEXT CALCULATE PH OF BOTTOMS AT 100
       COUNT = 0
       LO = 0!
       HI = 14!
       MARK1:
       PHT = (HI + LO)/2
       HT = EXP(- LTEN*PHT)
       X = KAH*HT
        FUNCT = HT + NF*X/(THEB*(1+X) + THEO*BETA) - AB -KWH/HT
       IF FUNCT > 0 GOTO JUMP
       HI = PHT
```

```
        GOTO HOP
       JUMP:
        LO = PHT
       HOP:
        COUNT = COUNT + 1
        IF COUNT < CMAX GOTO MARK1
        PHB = (HI + LO)/2
        HBH = EXP(- LTEN*PHB)
REM --- HBH IS THE HYDROGEN ION CONCENTRATION IN THE BOTTOMS AT 100
REM --- NOW DETERMINE THE NH3-NH4 CONCENTRATION ,NB ,IN THE BOTTOMS
         'AND, NO, IN THE OVERHEADS
       X = KAH*HBH
        NB = NF*(1!+X)/(THEB*(1!+X) + THEO*BETA)
       NO = NB*BETA/(1!+X)
REM --- NOW CALCULATE THE PH OF THE OVERHEADS ,PHO AT 25
        COUNT = 0
        LO = 0!
        HI = 14!
        MARK2:
        PHT = (HI + LO)/2
        HT = EXP(- LTEN*PHT)
        X = KAC*HT
         FUNCT = HT + NO*X/(1!+X) -KWC/HT
        IF FUNCT > 0 GOTO JUMP2
        HI = PHT
        GOTO HOP2
        JUMP2:
        LO = PHT
        HOP2:
        COUNT = COUNT + 1
        IF COUNT < CMAX GOTO MARK2
        PHO = (HI + LO)/2
        HOC = EXP(- LTEN*PHB)
 REM --- NOW CALCULATE THE PH OF THE BOTTOMS AT 25
        COUNT = 0
        LO = 0!
        HI = 14!
        MARK3:
        PHT = (HI + LO)/2
        HT = EXP(- LTEN*PHT)
        X = KAC*HT
         FUNCT = HT + NF*X/(THEB*(1+X) + THEO*BETA) - AB -KWH/HT
        IF FUNCT > 0 GOTO JUMP3
        HI = PHT
        GOTO HOP3
        JUMP3:
        LO = PHT
        HOP3:
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```
      COUNT = COUNT + 1
        IF COUNT < CMAX GOTO MARK3
        PHBC = (HI + LO)/2
        HBC = EXP(- LTEN*PHBC)
 REM --- PHBC IS THE PH OF THE BOTTOMS AT 25  AND HBC IS THE CORRESPONDING H+ CONC.
 REM --- NEXT WE PRINT OUT RESULTS
PRINT
PRINT
PRINT  "FRACTION OF FEED GOING TO BOTTOMS = ", THEB
PRINT " INITIAL NH3 -NH4  MOLALITY =            ", NF
PRINT " INITIAL PH OF FEED  =                   ", PHF
PRINT
PRINT  "MOLALITY OF NH3 IN THE OVERHEADS = " ,NO
PRINT  " THE  PH OF THE OVERHEADS AT 25°C = " ,PHO
PRINT
PRINT  " THE MOLALITY OF NH3-NH4 IN THE BOTTOMS  = ", NB
PRINT  " THE PH OF THE BOTTOMS AT 25°C = " ,PHBC
LPRINT  "FRACTION OF FEED GOING TO BOTTOMS = ", THEB
LPRINT " INITIAL NH3 -NH4  MOLALITY =            ", NF
LPRINT " INITIAL PH OF FEED  =                   ", PHF
LPRINT
LPRINT  "MOLALITY OF NH3 IN THE OVERHEADS = " ,NO
LPRINT  " THE  PH OF THE OVERHEADS AT 25C = " ,PHO
LPRINT
LPRINT  " THE MOLALITY OF NH3-NH4 IN THE BOTTOMS  = ", NB
LPRINT  " THE PH OF THE BOTTOMS AT 25C = " ,PHBC
LPRINT
INPUT WHAT

END
```

APPENDIX 2

Calculation of Ka at 100°C for NH_3-NH_4^+ Aqueous Equilibrium

$$NH_3 + H^+ \rightleftharpoons NH_4^+$$

$$Ka = [NH_4^+]/[NH_3][H^+]$$

T, °C	Log Ka, obs.[a]	ln Ka, obs.	ln Ka, calc.[b]
0	10.081	23.212	23.217
5	9.904	22.805	22.303
10	9.731	22.406	22.403
15	9.564	22.022	22.018
20	9.400	21.644	21.646
25	9.245	21.287	21.287
30	9.093	20.937	20.939
35	8.947	20.601	20.603
40	8.805	20.297	20.278
45	8.670	19.963	19.963
50	8.539	19.662	19.658
100			17.063

[a] See Reference (2)

[b] Calculations made from the expression

$$\mathbf{\ln K = -2.98026 + 6424.28(1/T) + 0.47747 \ln T}$$

where constants were obtained by regression analysis of ln Ka, 1/T (°K), and ln T(°K) for the observed Ka values at 0-50°C.

Note: $Kw = [H^+][OH^-]$ at 100°C is 5.508 E-13

log Kw at 100°C = -12.259; Kw = 5.508 E-13

APPENDIX 3

Calculation of Kp at 100°C for $NH_3(aq) \rightleftharpoons NH_3(g)$

$Kp = P_{NH3}(atm)/[moles\ NH_3/kg\ H_2O] = 0.227\ (atm)/[moles\ NH_3/kg\ H_2O]$

T, °C	Log Kp, obs.[a]	ln Kp, obs.	ln Kp, calc.[b]
0	-2.288	-5.269	-5.310
10	-2.074	-4.777	-4.773
20	-1.872	-4.311	-4.280
30	-1.669	-3.843	-3.827
40	-1.463	-3.368	-3.410
50	-1.304	-3.003	-3.024
60	-1.170	-2.695	-2.668
70			-2.338
80			-2.031
90			-1.747
100			-1.483

[a] See Reference (3)

[b] Calculations made from the expression

$$\ln K = 51.881 - 5915.37(1/T) - 6.334 \ln T$$

where constants were obtained by regression analysis of ln Kp, 1/T(°K), and ln T(°K) for the observed Ka values at 0-60°C.

APPENDIX 4

Calculation of the pH in the Final Effluent Stream

$N_s = [F_{ix}N_{ix} + F_oN_o]/F_s$ (See Equation 3)

where the symbols s, ix, and o refer to the final, ion exchange effluent, and overhead streams, respectively. (See Fig. 1) Based on the maximum and average concentration for total NH_4^+/NH_3 species[1], presuming a Df of 19 across reverse osmosis, of 1.79 E-4 M and 5.00 E-5 M, repectively,

$N_{s(max)}$ = [(148 gpm)(1.79 E-4 M) + (18 gpm)(6.53 E-5 M)]/(166 gpm)
= 1.67 E-4 M , and

$N_{s\ (ave)}$ = [(148 gpm)(5.00 E-5 M) + (18 gpm)(6.53 E-5 M)]/(166 gpm)
= 5.17 E-5 M.

The concentration of anion associated with NH_4^+ in the final stream, $A_s = F_{ix}A_{ix}/\ F_s = [(148\ \text{gpm})A_{ix}]/166\ \text{gpm}$

$A_{s(max)}$ = 1.60 E-4 M, and

$A_{s(ave)}$ = 4.46 E-5 M,

where $A_{ix(max)}$ = 1.79 E-4 M and $A_{ix(ave)}$ = 5.00 E-5 M.

$Ka = A_s/[H^+][N_s - A_s]$ (See Equation 4)

$[H^+]_{(max)} = A_s/\ Ka\ [N_s - A_s]$ = (1.60 E-4 M)/(1.76 E+9)(7.0 E-6 M)
= 1.30 E-8 M

$[H^+]_{(ave)} = A_s/\ Ka\ [N_s - A_s]$ = (4.48 E-5 M)/(1.76 E+9)(7.1 E-6 M)
= 3.59 E-9 M

pH = 7.9 (max)
= 8.4 (ave)

TABLE 1

Calculated pH and NH_3 Concentrations in the F/H ETF Evaporator System[a]

pH, 25°C			NH_3/NH_4^+ molality	
Initial Feed	Bottoms	Overheads	Overheads	Bottoms
4.5	3.5	9.3	4.2 E-5	8.3 E-2
5.0	3.9	9.4	5.2 E-5	8.2 E-2
5.5	4.1	9.4	5.6 E-5	8.2 E-2
6.0	4.2	9.4	5.8 E-5	8.2 E-2
6.5	4.5	9.4	6.5 E-5	8.2 E-2
7.0	5.0	9.5	8.8 E-5	8.2 E-2
7.5	5.4	9.7	1.8 E-4	8.1 E-2
8.0	5.9	9.9	5.0 E-4	7.8 E-2
8.5	6.4	10.2	1.4 E-3	7.0 E-2
9.0	6.9	10.4	3.3 E-3	5.3 E-2

[a] Initial NH_3/NH_4^+ molality = 0.0083 molal[1]
Fraction of feed going to bottoms = 0.1

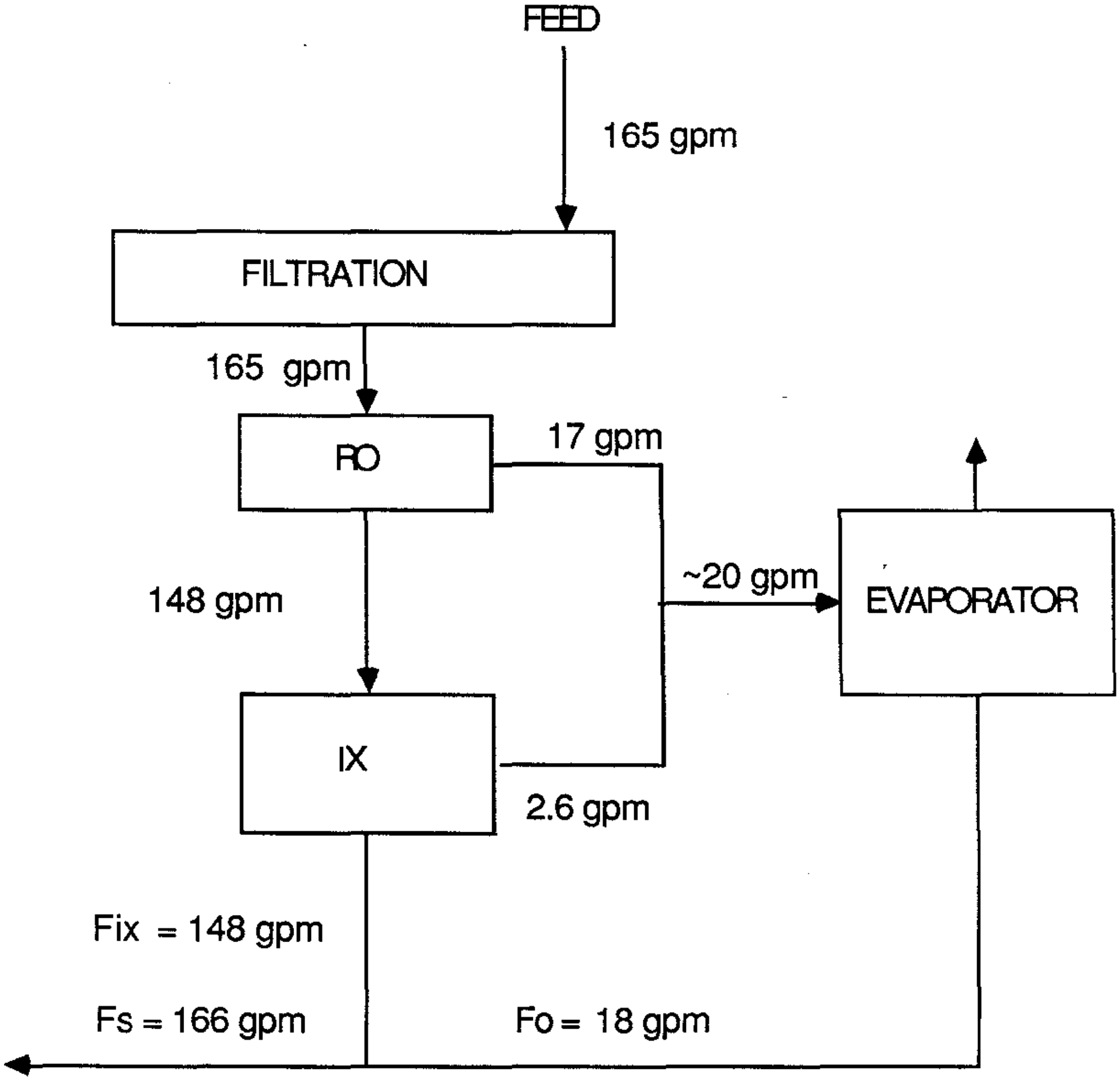

FIGURE 1

A SCHEMATIC OF THE F/H ETF