FRACTIONAL CRYSTALLIZATION
OF
HANFORD WASTE

Don Geniesse, Presenter
INTRODUCTION

• HANFORD WASTE CONTAINS THE MAJORITY OF ELEMENTS, MANY ISOTOPES, AND SEVERAL OXIDATION STATES – A TOTAL OF 1,600 ESP SPECIES

• FRACTIONAL CRYSTALLIZATION CAN SEPARATE COMMON SODIUM SALTS (NaNO$_3$, Na$_2$SO$_4$, Na$_2$CO$_3$) FROM THE BULK OF SOLUBLE RADIOACTIVE COMPONENTS (Cs, Tc, I) FOR LAW TREATMENT

• FRACTIONAL CRYSTALLIZATION FLOWSHEET MODELED & OPTIMIZED USING ESP
WATER ANALYZER USED TO RECONCILE ANALYTICAL DATA

• CHARGE BALANCE

• FREE HYDROXIDE BALANCE FOR ALUMINUM SOLUBILITY

• PHASE CONTACT STUDIES TO DETERMINE SOLIDS BASED ON SOLUBILITY (i.e. Fe(OH)$_3$, FeOOH, Fe$_2$O$_3$)

• REDOX SURVEYS TO DETERMINE OXIDATION STATES (i.e. Cr, Mn, Hg, Co)
AY102 REDOX SURVEY

ORP

CONCENTRATION

N(+2)  N(+3)  N(+5)  PU(+4)  PU(+5)  PU(+6)  HG(0)  HG(+2)  AG(0)  AG(+3)  MN(+2)  MN3O4PPT  MN(+3)  MN(+4)  MN(+6)  MN(+7)  CO(+2)  CO3O4PPT  CEO2PPT  CE(+3)AQUE  RHIIIOH2ION  RH2O3PPT  RH(+2)AQUE
EVAPORATION SURVEYS

- EVAPORATION SURVEYS GRAPH IONIC ACTIVITY DATA, SOLUBILITY PRODUCTS, IONIC STRENGTH, AND PRECIPITATION CURVES
- USED TO DETERMINE OPTIMUM CRYSTALLIZATION TEMPERATURE AND EXTENT OF EVAPORATION
EVAPORATION SURVEY
CASE 5

H2O EVAPORATED (gms)

ln a or PRECIPITATED SOLIDS (gms)

IONIC STRENGTH

αNa+
αSO4-2
αCO3-2
αNO3-1
αOH-1
αAl(OH)4-1
αH2O
KNa6(SO4)2CO3
KNa2CO3.1H2O
KNaNO3
KNaAlO2
KAl(OH)3
Na6(SO4)2CO3(s)
Na2CO3.1H2O(s)
NaNO3(s)
Na2Al2O4.2½H2O(s)
Al(OH)3(s)

IONIC STRENGTH

An AREVA Group Company

COGEMA
ENGINEERING CORP.
An AREVA Group Company
THREE-DIMENSIONAL SURVEYS ARE USED TO DETERMINE OPERATING LINE FOR CRYSTALLIZATION
MAINTAINING ALUMINUM SOLUBILITY IS VERY IMPORTANT DURING SALT CRYSTALLIZATION

• SLOW ALUMINUM CRYSTALLIZATION KINETICS

• ALUMINUM MAY FORM AMORPHOUS Al(OH)₃ GEL IF GIBBSITE SOLUBILITY IS EXCEEDED

• ALUMINUM SOLUBILITY CONTROLLED BY MAINTAINING IAP’s OF Al(OH)₃ & NaAlO₂ EQUAL DURING CRYSTALLIZATION
ESP FLOWSHEET MODELS ARE USED TO SIMULATE FRACTIONAL PROCESS TO DETERMINE:

- THEORETICAL CRYSTALLIZATION YIELDS
- MAXIMUM RECYCLE RATES
- EXTENT OF DECONTAMINATION
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<td>3</td>
<td>SULFUR</td>
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<td>4</td>
<td>OVERFLOW</td>
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<td>5</td>
<td>HYDROCYCLONE</td>
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<td>6</td>
<td>PURGE MIX</td>
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**Analysis:**

- **Dry Feed**
  - **Solids:** 1,170 g
  - **Water:** 519.5 g
- **Crystalizer**
  - **Solids:** 620 g
  - **Water:** 1,230 g
- **Sulfur**
  - **Solids:** 406 g
  - **Water:** 1,230 g
- **Overflow**
  - **Solids:** 1,000 g
  - **Water:** 1,549 g
- **Hydrocyclone**
  - **Solids:** 310 g
  - **Water:** 8.46 g
- **Purge Mix**
  - **Solids:** 25 g
  - **Water:** 51.95 g

**Further Analysis:**

- **Liquid Density:** 1,170 g
- **Velocity:** 1,140 g
- **Joule Strength:** 1,080 g
- **Solution:** 1,080 g
- **Liquid:** 1,080 g
- **Spent Wash:** 1,080 g
- **Cesium in Product:** 1,170 g
- **Dil_H2O:** 1,140 g

**Additional Details:**

- **Recovery Ratio:** 1,170 g
- **Sodium Increase:** 1,140 g
- **Theoretical Yields:** 1,080 g
- **Na:** 1,080 g
- **CO3:** 1,080 g
- **NO3:** 1,080 g
- **Al:** 1,080 g
- **Cs:** 1,080 g
CONCLUSIONS

HANFORD WASTE CHEMISTRY IS HIGHLY COMPLEX

ESP CAN BE USED:

• TO RECONCILE WASTE ANALYSIS
• PERFORM REDOX AND EVAPORATION SURVEYS
• FLOWSHEET PROPOSED FRACTIONAL CRYSTALLIZATION PROCESS