Radiolytic Treatment of the Next-Generation Caustic-Side Solvent Extraction (NGS) Solvent and its Effect on the NGS Process

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Supplementary Information

INTRODUCTION

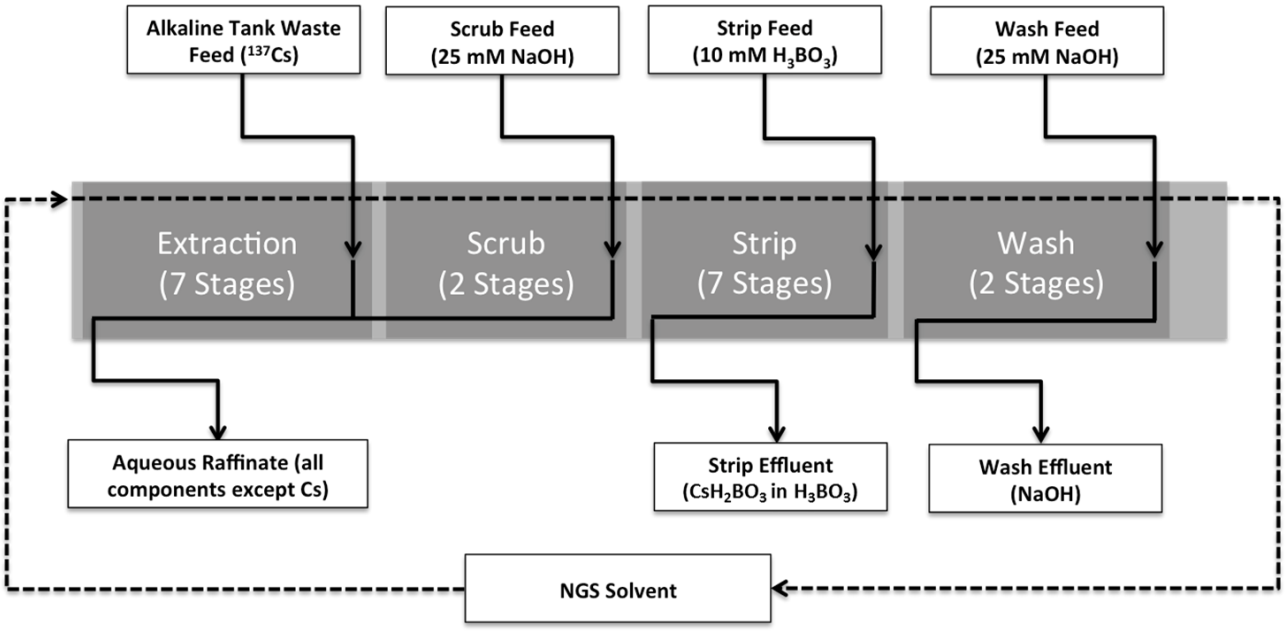

Figure 1: NGS Flowsheet for the Modular CSSX Unit (MCU) at Savannah River Site (SRS).[1]

EXPREIMENTAL

Table 1. Constituent ions of the tank waste simulant SRS-15[2]

Analyte or Species	SRS-15 mol/L
Principal constituents:	
Al as ($Al(OH)_4^-$)	0.280
Cl^-	2.4×10^{-2}
CO_3^{2-} (TIC)	0.150
Cs^+ (Total)	1.4×10^{-4}
K^+	0.015
Na^+	5.60
NO_2^-	0.500
NO_3^-	2.03
OH^- (Free)	2.06
SO_4^{2-}	0.140
Minor inorganic constituents:	
Ag(I)	9.3×10^{-8}
CrO_4^{2-}	1.4×10^{-3}
Cu(II)	2.3×10^{-5}
F^-	2.8×10^{-2}
Fe(III)	2.6×10^{-5}
Hg(II)	2.5×10^{-7}
MoO_4^{2-}	7.0×10^{-5}
NH_3	1.0×10^{-3}
Pb(II)	1.0×10^{-5}
Pd(II)	3.8×10^{-6}
PO_4^{3-}	7.0×10^{-3}
Rh(III)	2.0×10^{-6}
Ru(III)	8.1×10^{-6}
Si(IV)	3.0×10^{-2}
Sn(II)	2.0×10^{-5}
Minor organic constituents:	
n-Butanol	2.7×10^{-5}
Tri-*n*-butylphosphate (TBP)	1.9×10^{-6}
Di-*n*-butylphosphate (DBP)	1.2×10^{-4}

Mono-*n*-butylphosphate (MBP)	1.6×10^{-4}
Formate (HCO_2^-)	3.3×10^{-2}
Oxalate ($C_2O_4^{2-}$)	8.0×10^{-3}
Trimethylamine	1.7×10^{-4}

Absorbed Dose Calculation.

The original activity of the ^{60}Co source was 24,000 Ci in 1977. At the time of installation, the dose rate (D_0) was determined to be 18,500 Gy/h. The half-life ($t_{1/2}$) of ^{60}Co is 5.27 y, which is used to calculate the current dose rate. Using Eq. 1, Samples were analyzed at 2500, 5000, 10,000, 25,000, and 50,000 Gy. The length of irradiations was calculated by simply dividing the desired dose by the dose rate, *R*.

$$R = R_0 e^{-0.693t/t_{1/2}} \quad (1)$$

Table 2. Defined doses and calculated exposure times

Dose (kGy)	2.5	5	10	25	50
Contact duration (h)	11	22	44	110	220

Gas Chromatography Machine Settings

For the 6850/FID instrument, the inlet was set to splitless injection. The injection port was set at a temperature of 280ºC. The column used was an Agilent HP-5MS (5% phenyl methyl siloxane) open-

capillary column with a 30 m length, 0.25 cm inner diameter, and stationary-phase thickness of 0.25 μm. The carrier gas was H_2, set in constant flow mode at 2.2 mL/min (a nominal head pressure of 14.30 psi, to give an average linear velocity of 60 cm/sec). The detector was set at 300 ºC, with an H_2 flow of 50 mL/min, a compressed air flow of 450 mL/min, and no make-up gas. For the 5890/MS instrument, the injection port was set at a temperature of 250 ºC. The column used was a J&W HP-5MS (5% Phenyl methyl siloxane) open capillary column with an approximate length of 25 m, 0.25 cm inner diameter, and stationary-phase thickness of 0.25 μm. The GC used He as the carrier gas, set in constant flow mode at 1 mL/min. The detector was set at 280ºC.

For the analysis of DCiTG in an organic solvent such as CH_2Cl_2, the product, reactants, and crude reaction mixtures were analyzed using the following temperature program: 100 ºC ramped at 20ºC/min to a final temperature of 300ºC, then held at 300ºC for three min. The integrator was started at 2.5 min and recorded signal to the end of the run. For the analysis of the NGS solvent, the integrator was started at 8.5 min and recorded the signal until the end of the run so that the much more intense signals from the Isopar solvent and the modifier alcohol were ignored.

REFERENCES

1. Leonard, R., *Initial Flowsheet for the Next Generation CSSX Process in the MCU. Report for FY2010*, ANL-LTR-NGCSSX-001, Argonne National Laboratory, 2010.
2. Peterson, R. A. *Preparation of Simulated Waste Solutions for Solvent Extraction Testing*, WSRS-RP-2000-00361, Westinghouse Savannah River Company, 2000.