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DWPF Coal-Carbon Waste Acceptance Criteria Limit Evaluation (Tank 48 Impact Study)

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EXECUTIVE SUMMARY

A paper study was completed to assess the impact on the Defense Waste Processing Facility (DWPF)'s Chemical Processing Cell (CPC) acid addition and melter off-gas flammability control strategy in processing Sludge Batch 10 (SB10) to SB13 with an added Fluidized Bed Steam Reformer (FBSR) stream and two Salt Waste Processing Facility (SWPF) products (Strip Effluent and Actinide Removal Stream). In all of the cases that were modeled, an acid mix using formic acid and nitric acid could be achieved that would produce a predicted Reducing/Oxidizing (REDOX) Ratio of 0.20 $Fe^{+2}/\Sigma Fe$. There was sufficient formic acid in these combinations to reduce both the manganese and mercury present. Reduction of manganese and mercury are both necessary during Sludge Receipt and Adjustment Tank (SRAT) processing, however, other reducing agents such as coal and oxalate are not effective in this reduction. The next phase in this study will be experimental testing with SB10, FBSR, and both SWPF simulants to validate the assumptions in this paper study and determine whether there are any issues in processing these streams simultaneously.

The paper study also evaluated a series of abnormal processing conditions to determine whether potential abnormal conditions in FBSR, SWPF or DWPF would produce melter feed that was too oxidizing or too reducing. In most of the cases that were modeled with one parameter at its extreme, an acid mix using formic acid and nitric acid could be achieved that would produce a predicted REDOX of 0.09-0.30 (target 0.20). However, when a run was completed with both high coal and oxalate, with minimum formic acid to reduce mercury and manganese, the final REDOX was predicted to be 0.49 with sludge and FBSR product and 0.47 with sludge, FBSR product and both SWPF products which exceeds the upper REDOX limit. The following cases were considered and the results reported below:

1. **Low Formate Destruction.** Even with no formate destruction in the SRAT or SME, there was enough formic acid added to reduce Mn and Hg and produce a REDOX of 0.20 $Fe^{+2}/\Sigma Fe$.
2. **High FBSR Coal Concentration.** High concentrations of FBSR coal will produce a melter feed with a predicted REDOX of 0.20. But insufficient formic acid is added to reduce both manganese and mercury unless acid stoichiometry is increased.
3. **High Actinide Removal Product (ARP) oxalate Concentration.** The ARP oxalate contributes <0.01% of the carbon. Even a large increase of oxalate from the SWPF stream will have minimal impact on REDOX.
4. **High Nitrate Destruction.** In the baseline analysis, it was assumed that 2.6% of the nitrite was converted to nitrate. This factor has varied from -30% to 33% in CPC Experiments. A test case was completed assuming maximum catalytic activity to form ammonia and a -30% nitrite to nitrate conversion in the SRAT (all nitrate destroyed, no nitrate generation, 30% of nitrite reduced to ammonia) and 20% nitrate destruction in the Slurry Mix Evaporator (SME). Even under these extreme conditions, the acid mix can be adjusted to produce a predicted REDOX of 0.20. Low initial nitrate concentration in the feeds to the DWPF CPC leads to the same issue as high nitrate destruction.
5. **High SWPF Organic Concentration.** The SWPF organic from solvent extraction is very small compared to the coal in the FBSR. In addition, most of the organic is removed during boiling in the CPC, so very little organic will be present in the melter feed so there should be minimum impact.
6. **High Coal, Oxalate, SWPF Organic Concentration:** In this case, if enough formic acid is added to reduce the manganese and mercury, the resulting REDOX is more reducing than is typically targeted and may lead to more Ni, Cu and noble metal reduction in the

melter. A REDOX of 0.20 can not be achieved with any formic acid/nitric acid mixture unless acid stoichiometry is increased.

7. **High Acid Stoichiometry.** DWPF often targets 120-150% Koopman acid stoichiometry to maximize the nitrite destruction rate and the mercury stripping. A REDOX of 0.20 can be achieved; however the Total Organic Carbon (TOC) concentration in the melter feed is approximately 18,000 mg/kg, approaching the DWPF limit of 18,500 mg/kg.
8. **High Sludge Oxalate.** A high sludge oxalate concentration is possible if oxalic acid is used in tank cleaning. Current planning is to destroy the oxalate prior to sludge washing. In case the oxalate destruction process is inadequate or delayed, a test case was completed with 10,000 mg/kg oxalate in sludge. A REDOX of 0.20 can be achieved; however the TOC concentration in the melter feed is approximately 17,900 mg/kg, approaching the DWPF limit of 18,500 mg/kg.

A total of six cases were considered in the assessment of DWPF melter off-gas flammability using two computer models that describe the cold cap chemistry and the off-gas combustion and dynamics. The baseline sludge chosen was SB10 at 100% and 150% acid stoichiometry. Coal was then added to these SB10 variations until either the current TOC limit of 18,900 ppm or the flammability safety basis limit of 60% of the LFL was exceeded. The results of model runs show that if: (1) an administrative control is put in place on glass redox, (2) coal particles remain well dispersed, and (3) the concentration of coal can be accurately measured, considerably greater than 7,441 ppm of coal may be added to the DWPF melter feed. On the other hand, if coal is added to the redox-adjusted SB10 at 100-150% acid stoichiometry without giving further consideration to the redox control, the maximum amount of coal that can be added without exceeding the 60% of the LFL safety basis limit is estimated to be ~5,000 ppm.

The assumptions made in performing these calculations need to be validated in the CPC with all four streams present and with the level of coal currently projected in the FBSR product. After this series of testing is completed, the melter off-gas flammability calculations should be repeated to validate the assumptions and also to consider the impact of the melter bubblers.

The worst case sludge batch for this analysis was SB10. The sludge for future testing should be a SB10 simulant. The predicted sludge includes monosodium titanate (MST) which will be added from the actinide removal process in SWPF. To prevent overestimating the MST present, the sludge composition for simulant production will be recalculated by removing the MST and renormalizing the remaining sludge components.

The results of this feasibility analysis indicate that the processing of SB10-13 sludge together with the FBSR product using a coal concentration of 15 wt % and SWPF products is possible in the CPC. A targeted REDOX of 0.2 is possible and the melter total organic carbon limit should be maintained. In addition, FBSR product produced in Hazen testing will be used along with ARP/ Modular Caustic Solvent Extraction Unit (MCU) simulants used in previous studies. No organic will be added to the MCU simulant and data from previous testing will be used to provide expected concentration in the melter feed.

It is also recommended that the high coal content in the FBSR product should be re-evaluated. If FBSR product with 15 wt% coal-carbon is combined with sludge and processed in the CPC, the CPC product approaches the TOC limit for CPC processing. Minimizing the coal-carbon concentration will also limit the nonradioactive impurities added in waste processing (coal ash, carbon, sulfur, etc.). This preliminary study should be reassessed when a new CPC flowsheet is defined and when the FBSR product stream is finalized.

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LIST OF ABBREVIATIONS

CPC	Chemical Processing Cell
DOE-SR	Department of Energy – Savannah River
DWPF	Defense Waste Processing Facility
FBSR	Fluidized Bed Steam Reformer
ICP	Invariant Condensed Phase
MCU	Modular Caustic Solvent Extraction Unit
MOG	Melter Off-Gas
PTD	Product Dissolution Tank
REDOX	Reduction/Oxidation Potential (Ratio of $Fe^{+2}/\Sigma Fe$)
SB	Sludge Batch
SME	Slurry Mix Evaporator
SRAT	Sludge Receipt and Adjustment Tank
SRNL	Savannah River National Laboratory
SRNS	Savannah River Nuclear Solutions
SRR	Savannah River Remediation, LLC
SRS	Savannah River Site
SWPF	Salt Waste Processing Facility
TIC	Total Inorganic Carbon
TOC	Total Organic Carbon
TPB	Tetraphenylborate
TT&QAP	Task Technical and Quality Assurance Plan
TTR	Technical Task Request
WAC	Waste Acceptance Criteria

1.0 Introduction

Currently Tank 48 has approximately 250,000 gallons of legacy waste containing organic potassium and cesium (K and Cs) tetraphenyl borate (TPB) solids from the In-Tank Precipitation (ITP) project. The waste is incompatible with other Tank Farm treatment operations. The tank has been isolated from the Tank Farm service since 1998. In order to make space in the Savannah River Site (SRS) Tank Farm, the Tank 48 waste must be processed to eliminate its organic content for downstream processing, including Tank Farm and Defense Waste Processing Facility (DWPF) processes. On June 10, 2009, the Department of Energy-Savannah River (DOE-SR) concurred with Savannah River Remediation (SRR) Business Decision Recommendation to select the THOR® sodium carbonate based Fluidized Bed Steam Reforming (FBSR) technology to treat the Tank 48 waste.[1]The FBSR processing of the Tank 48 content is expected to be completed over a two-year period from 2014 to 2016.

The FBSR process will treat the Tank 48 organic laden waste and generate organic free sodium carbonate based solid. The solids product will be slurried with water and sent to the Tank Farm for further processing. In the Tank Farm, the FBSR product slurry will be combined with sludge, washed as part of the sludge preparation process, and fed to DWPF. The FBSR product slurry will be blended with other sludge tanks to produce Sludge Batches 10-13 (SB10-SB13). Current projections of SB10-SB13[2] combined with expected composition of the FBSR product[3] will be used to predict the resulting sludge composition for SB10-SB13.

DWPF will process the washed sludge concurrently with two products from salt waste, the cesium rich strip effluent stream and the actinide rich actinide removal product from the Salt Waste Processing Facility (SWPF). Both of these streams contain organic species that must be accounted for in the requested analysis. Until the SWPF begins processing, the products from the Actinide Removal Process (ARP) and the Modular Caustic-Side Solvent Extraction Unit (MCU) will be used. These streams will be defined as salt processing streams in the rest of the report.

DWPF targets the production of a melter feed that has a balanced REDOX (defined as 0.2 $Fe^{+2}/\Sigma Fe$). An acceptable REDOX range is 0.09-0.30. It accomplishes this by using a blend of formic acid and nitric acid using a REDOX algorithm[4] shown in Eq. (1) below. If the melter feed is too reducing (REDOX >0.3), metals such as copper, nickel and the noble metals can become reduced, accumulate in the bottom of the melter, and short out the electrodes, shortening the life of the melter. If the melter feed is too oxidizing (REDOX <0.09), the glass will release oxygen, causing melter foaming, pressure upsets, and slowing melt rate.

$$REDOX=0.2358+0.1999*((2*C_{formate}+4*C_{oxalate}+4*C_{Carbon}-5*(C_{Nitrate}+C_{Nitrite})-5*C_{Mn}))*(45/TS) \quad (1)$$

Where C = species concentration, g-mole/kg melter feed, TS = total solids in melter feed in wt %, and REDOX is a molar ratio of $Fe^{+2}/\Sigma Fe$

The FBSR process uses coal-carbon as a reaction additive for promoting a reducing environment in the reformer as well as for maintaining the process in an auto-thermal mode. Some levels of coal-carbon (@100% carbon) will be present in the FBSR product slurry to the Tank Farm and DWPF processing. The purpose of this study is to estimate a coal-carbon limit in the FBSR product for DWPF sludge receipt to ensure the sludge can be safely processed without exceeding the DWPF melter off-gas (MOG) flammability safety basis.

Tank 48 contains a high organic concentration, due mainly to the potassium tetraphenylborate present. Approximately 40,000 lb of tetraphenylborate carbon is currently present in Tank 48. Processing of the waste in the FBSR will produce approximately 80,000 lb of carbon in the form of carbonate and another 120,000 lbs of carbon in the form of residual coal. Neither the carbon from coal or carbonate will wind up in the final glass waste form but may impact processing in DWPF and could lead to pluggage during CPC sampling and transferring due to the large particle size (10% greater than 177 μm) of the FBSR product.

DWPF produces a melter feed product that has a balanced REDOX (defined as 0.2 $Fe^{+2}/\Sigma Fe$). It accomplishes this by using a blend of formic acid and nitric acid to control REDOX. DWPF uses a REDOX algorithm[5] to control the quantities. If the melter feed is too reducing, metals such as copper, nickel and the noble metals can become reduced, accumulate in the bottom of the melter, and short out the electrodes, shortening the life of the melter. If the melter feed is too oxidizing, the glass will release oxygen, causing melter foaming, pressure upsets, and slowing melt rate.

The FBSR process uses coal-carbon as a reaction additive for promoting a reducing environment in the reformer as well as for maintaining the process in an auto-thermal mode. Some levels of coal-carbon (@100% carbon) will be present in the FBSR product slurry to the Tank Farm / DWPF processing. The purpose of this study is to estimate a coal-carbon limit in the FBSR product for DWPF sludge receipt to ensure the sludge can be safely processed without impacting the DWPF safety basis. The primary products of this study are the results of the off-gas flammability assessment for the DWPF melter and the Chemical Processing Cell (CPC) demonstrations with simulant, which will provide an estimate of the total organic carbon (TOC) limit along with the associated coal-carbon limit. It should be noted that the TOC varies from sludge batch to sludge batch due to composition changes in oxalate, coal-carbon, and other carbon sources but the main contributor to the TOC in the melter feed is the formate salts originating from the addition of formic acid.

Tank 48 Projects Engineering (TPE) of Savannah River Remediation (SRR) has requested this demonstration via Technical Task Request (TTR) X-TTR-H-2009-00006.[6] The scope of the study is being controlled with the Task Technical and Quality Assurance Plan (TT&QAP).[7]

This work is Technical Baseline Research and Development (R&D) for an onsite customer (Tank 48 and DWPF).

2.0 Experimental Procedure

No experimental work was completed in this phase of the testing.

3.0 Results and Discussion

Four waste streams will be added to the DWPF CPC once the FBSR begins processing the Tank 48 contents. The four streams and their expected volumes are summarized in Table 3-1. As part of this study, it was assumed that DWPF will be producing 325 canisters per year (1.25 million lb/yr of glass) using the current DWPF chemical processing flowsheet and that the FBSR and salt streams will be processing at design capacity. In addition, it is assumed that no other processing facilities are providing waste to DWPF.

Table 3-1. DWPF Processing Streams during FBSR Processing

Waste Stream	Annual Production Rate, gal/yr	Primary carbon source
Sludge	Depends on sludge batch	Carbonate, oxalate
FBSR Product Dissolution Tank (PDT)	160,000	Unreacted Coal, carbonate
Strip Effluent	564,000	Solvent (Isopar, modifier, extractant)
Actinide Removal Stream	121,000	Oxalate, carbonate

Note that the assumption of 325 canisters per year in DWPF is lower than the ultimate SRR plan of 400 canisters per year. At 325 canisters per year, 22% less sludge will be processed compared to 400 canisters per year. Since the FBSR processing rate is assumed constant, production at the higher throughput will effectively dilute the coal, leading to lower coal concentrations being fed into DWPF. However, if the 325 canister per year production rate can not be achieved, the coal-carbon concentration will be higher than estimated in this study. Also it should be noted that the sludge production rate (noted in the table above as “depends on sludge batch”) was calculated by difference, setting the SWPF and FBSR streams at their flowsheet targets, and calculating the volume of sludge that can be processed to achieve the 325 canister per year production rate.

The Hazen testing FBSR product[3] was between 9.3 and 17.1 wt % coal-carbon so 15% coal-carbon was used as a basis in this study. Coal is added in the FBSR product and some of this coal is unreacted and exits with the FBSR product. The coal in the 2008 Hazen product[3] was much higher than was measured in earlier processing. As a result, this study was initiated to develop waste acceptance criteria (WAC) to prevent a flammable mixture from forming in the DWPF melter offgas system.

Not all of the carbon fed to DWPF is fed to the melter. For example, formic acid, another carbon source, and nitric acid are added to the CPC to neutralize the waste. Neutralization of the waste destroys all of the carbonate and a portion of the oxalate. The addition of formic acid adds a large quantity of organic that will be fed to the melter. Also, volatile organics such as Isopar are steam stripped during processing so they do not reach the melter. However, the coal is inert during CPC processing and will be fed to the melter. The melter will oxidize all the remaining carbon to CO and CO_2 which may lead to a flammable offgas mixture if the carbon concentration in the melter feed is too high. The coal also adds other impurities that impact DWPF processing including hydrogen (impacts melter offgas flammability), sulfur, and coal ash. The coal composition of two coal sources used in FBSR testing is summarized in Table 3-2.[3] The ash content of the coal, similar to the solids present in sludge, is summarized in Table 3-3.

Table 3-2. Coal Composition

Component	Erwin	Bestac
Moisture	7.35	8.37
Ash	7.77	9.12
Al	0.81	1.26
Ca	0.17	0.14
Fe	0.15	0.44
K	0.01	0.03
Mg	0.06	0.01
Na	0.10	0.03
P	0.01	0.05
S	0.19	0.03
Si	2.14	2.59
Ti	0.04	0.04
Other	0.31	0.01
Carbon	80.45	78.59
Hydrogen	1.58	2.09
Oxygen*	1.69	0.39
Nitrogen	0.84	0.72
Sulfur	0.30	0.72
Total	100.00	104.63

Table 3-3. Coal Ash Composition

Component	Normalized SRNL Ash Analysis	
	2006 Erwin Ash@525 °C	2008 Bestac Ash@525 °C
Al_2O_3	19.63%	26.10%
CaO	2.99%	2.21%
Fe_2O_3	2.70%	6.91%
K_2O	0.13%	0.34%
MgO	1.24%	0.18%
Na_2O	1.69%	0.49%
P_2O_5	0.39%	1.15%
SO_4	7.50%	1.02%
SiO_2	58.91%	60.77%
TiO_2	0.76%	0.73%
Other	4.05%	0.10%
Total	100.00%	100.00%

3.1 Inputs

The expected composition of the four streams was provided by the Tank 48 project team[8]. Three of the streams are expected to remain relatively constant during the FBSR processing window, namely the two salt streams and the FBSR stream. It is likely that three or four different sludge batches will be processed during the FBSR processing window.

The information provided did not have all the information necessary for this study. As a result, a number of inputs needed to be calculated.

1. The FBSR product will be washed with the sludge batch processing in Tank 42 or Tank 51. In this study, an estimate was made of the composition of the FBSR product after washing to 1 M supernate sodium and 14 wt % insoluble solids. These are the approximate wash endpoints for the sludge processing. However, no attempt was made to duplicate the addition of multiple batch transfers of FBSR at various points in the washing cycle.
2. Estimates were made for slurry carbonate. An estimate of the slurry carbonate was made assuming the Ba, Ca, Mg and Pb were present as insoluble carbonates.
3. The total base (titration of the slurry to pH 7 with dilute HCl) was calculated by adding the amount of acid needed to neutralize the free hydroxide and aluminate.
4. Measurement of the calcined solids in the salt or FBSR streams was not available so they were estimated by converting the elemental solids as measured to the expected oxides and normalizing to 100%.

The two salt streams and the FBSR stream are summarized in Table 3-5. The four sludge batch compositions are summarized in Table 3-6. Note that the sludge estimate used in this study contained MST. This explains the higher Ti concentration in the runs without the SWPF runs than those with added SWPF (added MST). This does not impact the CPC calculations as MST is inert in the CPC models.

A number of the major assumptions are listed below:

1. Baseline DWPF flowsheet target 100% of acid stoichiometry predicted by Koopman Acid Demand Equation[9].
2. High concentrations of noble metals and mercury equivalent to SB6 predictions.
3. SWPF and FBSR processing at design basis rates.
4. Formic acid is needed for the reduction of Hg and Mn. Coal, oxalate, and other organic species will not reduce Hg and Mn so a minimum quantity of formic acid is needed for CPC processing.
5. High SRAT product total solids of 30 wt % because of the high concentration of solids in the sludge projections.

The following assumptions were necessary to complete the calculations (Table 3-4):

Table 3-4. CPC Processing Basis

Basis	Amount
Conversion of Nitrite to Nitrate in SRAT Cycle	2.60%
Destruction of Nitrite in SRAT and SME Cycle	100.00%
Destruction of Formic Acid Charged in SRAT	22.10%
Destruction of Oxalate Charged	50.00%
Percent Acid in Excess Stoichiometric Ratio	100.00%
SRAT Product Target Solids	30.00%
Nitric Acid Molarity	10.4
Formic Acid Molarity	23.55
REDOX Target	0.20
Trimmed Sludge Target Ag metal content, wt % solids basis	0.0142
Trimmed Sludge Target wt% Hg dry basis, wt % solids basis	3.9000
Trimmed Sludge Target Pd metal content, wt % solids basis	0.0066
Trimmed Sludge Target Rh metal content, wt % solids basis	0.0233
Trimmed Sludge Target Ru metal content, wt % solids basis	0.1121
Destruction of Formic Acid in SME	8.40%
Destruction of Nitrate in SME	11.90%
Assumed SME density, g/mL	1.420
Sludge Oxide Contribution in SME (Waste Loading)	40.00%
Target SME Solids total Wt%	50.0%

Table 3-5. Projected Composition of FBSR stream, and SWPF Actinide and Cesium Stream

Analysis or Estimate	**Actinide Stream**	**Cesium Stream**	**Washed FBSR**
Weight % Total Solids	10.09	0.21	18.50
Weight % Calcined Solids	7.28	0.17	13.66
Weight % Insoluble Solids	6.04	0.00	14.00
Weight % soluble Solids	4.05	0.21	4.50
Weight % supernate solids	4.31	0.21	5.23
Slurry Density, g/mL	1.06	1.00	1.06
Supernate density, g/mL	1.02	1.00	1.06
Anions, mg/kg slurry			
Nitrite (mg/kg)	3,181	0	28
Nitrate (mg/kg)	3,759	682	28
Formate (mg/kg)	55	0	0
Sulfate (mg/kg)	32	0	1,092
Chloride (mg/kg)	11	0	96
Phosphate (mg/kg)	27	0	259
Oxalate (mg/kg)	6,670	0	0
Slurry Total Inorganic Carbon (TIC)	2,558	0	6,465
Fresh Supernate TIC	2,786	0	7,517
Hydroxide (Base Equivalents) pH = 7, M	0.326	0.000	0.389
Coal/Carbon source, wt % total solids basis	0.0	0.0	41.6
Cations, wt % Calcined Solids Basis			
Al	11.89		1.35
Ba	0.28		0.04
Ca	2.96		3.35
Ce	0.69		0.00
Cr	0.32		0.00
Cu	0.11		0.01
Fe	33.00		1.44
K			1.77
La	0.26		0.00
Mg	0.39		0.04
Mn	4.39		0.04
Na	20.16		44.11
Ni	0.61		0.02
Pb	0.37		0.08
Si	4.03		10.53
S			0.44
Th	1.11		
Ti	1.97		1.58
U	2.05		
Zn	0.20		0.00
Zr	0.63		0.00

Table 3-6. Projected Composition of Sludge Batches SB10 to SB13

Analysis or Estimate	SB10	SB11	SB12	SB13
Weight % Total Solids	21.12	24.83	25.78	26.01
Weight % Calcined Solids	13.18	14.60	14.68	14.86
Weight % Insoluble Solids	13.13	15.28	15.82	15.95
Weight % soluble Solids	7.99	9.55	9.96	10.06
Weight % supernate solids	9.20	11.28	11.83	11.97
Slurry Density, g/mL	1.12	1.15	1.15	1.15
Supernate density, g/mL	1.03	1.04	1.04	1.04
Anions, mg/kg slurry				
Nitrite (mg/kg)	10,061	13,332	14,141	15,143
Nitrate (mg/kg)	6,958	9,283	9,860	10,491
Formate (mg/kg)	0	0	0	0
Sulfate (mg/kg)	288	440	474	275
Chloride (mg/kg)	12	14	17	11
Phosphate (mg/kg)	48	107	121	98
Oxalate (mg/kg)	0	0	0	0
Slurry Total Inorganic Carbon (TIC)	1,213	1,316	1,366	1,375
Fresh Supernate TIC	435	598	640	726
Hydroxide (Base Equivalents) pH = 7, M	0.640	0.467	0.422	0.383
Coal/Carbon source, wt % total solids basis	0.0	0.0	0.0	0.0
Cations, wt % Calcined Solids Basis				
Al	6.3	7.26	10.63	11.19
Ba	0.22	0.19	0.21	0.21
Ca	2.2	2.07	2.25	2.29
Ce	0.73	0.65	0.4	0.26
Cr	0.19	0.23	0.26	0.27
Cu	0.06	0.06	0.09	0.11
Fe	26.18	28.25	22.64	20.97
K	0.15	0.15	0.23	0.27
La	0.24	0.22	0.17	0.14
Mg	0.31	0.33	0.28	0.23
Mn	4.56	2.76	2.69	3.03
Na	19.77	18.71	18.68	18.47
Ni	0.76	0.4	0.27	0.37
Pb	0.39	0.33	0.21	0.16
Si	1.78	2.87	3.72	3.62
S	0.06	0.16	0.13	0.12
Th	2.54	0.71	0.01	0.01
Ti	1.37	1.47	1.51	1.5
U	1.31	0.66	1.46	2.66
Zn	0.06	0.19	0.15	0.19
Zr	0.46	0.43	0.48	0.49

3.2 CPC Processing Calculations to Predict Melter Feed Composition for Flammability Study

Calculations were completed to predict the melter feed composition for various CPC processing options to support the melter offgas flammability study. The SRNL acid calculation spreadsheet using the Koopman acid demand equation and Jantzen redox prediction[5] was used for these calculations.

3.2.1 *Typical CPC Processing*

Additionally, the volumes of the various streams needed to be estimated. In all cases, 325 canisters were produced per year or 1.25 million lb of glass. In the first case for each sludge batch, the sludge-only case, the mass of sludge necessary to produce 1.25 million lb of glass was calculated knowing the calcined solids concentration. In the second case, the FBSR washed product was combined with the sludge to produce 1.25 million lb glass. This included 1.16 million lb from the sludge and 0.09 million lb from the FBSR. In the third case, the FBSR washed product and both salt streams were combined with the sludge to produce 1.25 million lb glass. This included 1.07 million lb from the sludge and 0.09 million lb from the FBSR, 0.08 million lb from the Actinide stream and 0.001 million lb from the strip effluent stream.

The sludge only processing leads to the highest formate concentration. Processing of both sludge and the FBSR product leads to the highest coal-carbon concentration but much lower formate concentration. The combination of all four streams leads to the highest oxalate and coal-carbon concentration but lower formate concentration. The results from the CPC calculations are summarized in Table 3-7, Table 3-8, Table 3-9, and Table 3-10.

Table 3-7. SB10 CPC Processing Calculations (Predicted Melter Feed Composition)

Case Number	**SB10Tk48-1**	**SB10Tk48-2**	**SB10Tk48-3**
Case Description	SB10 Sludge Only	SB10 Tk48 FBSR No SWPF	SB10 Tk48 FBSR SWPF
Weight % Total Solids	50.00%	50.00%	50.00%
Weight % Calcined Solids	37.84%	37.31%	37.50%
Slurry Density	1.420	1.420	1.420
Anions, mg/kg slurry			
Nitrite (mg/kg)	0	0	0
Nitrate (mg/kg)	16,703	40,701	40,992
Formate (mg/kg)	39,901	24,005	24,323
Sulfate (mg/kg)	329	324	307
Chloride (mg/kg)	14	13	14
Phosphate (mg/kg)	54	53	54
Oxalate (mg/kg)	0	0	969
Slurry TIC (mg/kg)	0	0	0
Coal/Carbon source, mg/kg slurry	0	7,760	7,850
Total Carbon, mg/kg slurry basis	10,646	14,165	14,604
Cations, wt % Calcined Solids			
Al	2.51	2.50	2.66
B	1.49	1.49	1.49
Ba	0.09	0.09	0.09
Ca	0.88	0.87	0.89
Ce	0.29	0.29	0.29
Cr	0.08	0.08	0.08
Cu	0.02	0.02	0.03
Fe	10.42	10.39	10.58
K	0.06	0.06	0.06
La	0.10	0.10	0.10
Li	2.23	2.23	2.23
Mg	0.12	0.12	0.13
Mn	1.81	1.81	1.80
Na	11.43	11.40	10.85
Ni	0.30	0.30	0.30
Pb	0.16	0.15	0.15
Si	22.02	22.02	22.08
S	0.02	0.02	0.02
Th	1.01	1.01	0.97
Ti	0.55	0.54	0.56
U	0.52	0.52	0.54
Zn	0.02	0.02	0.03
Zr	0.18	0.18	0.19

Table 3-8. SB11 CPC Processing Calculations (Predicted Melter Feed Composition)

Case Number	**SB11Tk48-1**	**SB11Tk48-2**	**SB11Tk48-3**
Case Description	SB11 Sludge Only	SB11 Tk48 FBSR No SWPF	SB11 Tk48 FBSR SWPF
Weight % Total Solids	50.00%	50.00%	50.00%
Weight % Calcined Solids	36.74%	35.75%	36.31%
Slurry Density	1.420	1.420	1.420
Anions, mg/kg slurry			
Nitrite (mg/kg)	0	0	0
Nitrate (mg/kg)	15,790	43,227	43,701
Formate (mg/kg)	32,562	15,149	16,233
Sulfate (mg/kg)	293	290	275
Chloride (mg/kg)	12	12	13
Phosphate (mg/kg)	48	48	48
Oxalate (mg/kg)	0	0	953
Slurry TIC (mg/kg)	0	0	0
Coal/Carbon source, mg/kg slurry	0	8,854	8,951
Total Carbon, mg/kg slurry basis	8,688	12,895	13,542
Cations, wt % Calcined Solids			
Al	2.51	2.52	2.68
B	1.49	1.49	1.49
Ba	0.09	0.09	0.09
Ca	0.88	0.88	0.90
Ce	0.29	0.29	0.29
Cr	0.08	0.08	0.08
Cu	0.02	0.02	0.03
Fe	10.41	10.47	10.67
K	0.06	0.06	0.06
La	0.10	0.10	0.10
Li	2.23	2.23	2.23
Mg	0.12	0.12	0.13
Mn	1.81	1.82	1.82
Na	11.42	11.47	10.91
Ni	0.30	0.30	0.30
Pb	0.16	0.16	0.16
Si	22.02	22.03	22.09
S	0.02	0.02	0.02
Th	1.01	1.02	0.98
Ti	0.54	0.55	0.56
U	0.52	0.52	0.54
Zn	0.02	0.02	0.03
Zr	0.18	0.18	0.19

Table 3-9. SB12 CPC Processing Calculations (Predicted Melter Feed Composition)

Case Number	**SB12Tk48-1**	**SB12Tk48-2**	**SB12Tk48-3**
Case Description	SB12 Sludge Only	SB12 Tk48 FBSR No SWPF	SB12 Tk48 FBSR SWPF
Weight % Total Solids	50.00%	50.00%	50.00%
Weight % Calcined Solids	36.74%	36.17%	36.40%
Slurry Density	1.420	1.420	1.420
Anions, mg/kg slurry			
Nitrite (mg/kg)	0	0	0
Nitrate (mg/kg)	15,512	43,535	44,083
Formate (mg/kg)	31,728	14,032	15,210
Sulfate (mg/kg)	287	284	270
Chloride (mg/kg)	12	12	12
Phosphate (mg/kg)	47	47	48
Oxalate (mg/kg)	0	0	940
Slurry TIC (mg/kg)	0	0	0
Coal/Carbon source, mg/kg slurry	0	9,038	9,142
Total Carbon, mg/kg slurry basis	8,465	12,782	13,201
Cations, wt % Calcined Solids			
Al	2.49	2.51	2.67
B	1.49	1.49	1.49
Ba	0.09	0.09	0.09
Ca	0.87	0.88	0.90
Ce	0.29	0.29	0.29
Cr	0.08	0.08	0.08
Cu	0.02	0.02	0.03
Fe	10.35	10.42	10.62
K	0.06	0.06	0.06
La	0.09	0.10	0.10
Li	2.23	2.23	2.23
Mg	0.12	0.12	0.13
Mn	1.80	1.81	1.81
Na	11.38	11.43	10.88
Ni	0.30	0.30	0.30
Pb	0.15	0.16	0.15
Si	22.02	22.02	22.09
S	0.02	0.02	0.02
Th	1.00	1.01	0.97
Ti	0.54	0.55	0.56
U	0.52	0.52	0.54
Zn	0.02	0.02	0.03
Zr	0.18	0.18	0.19

Table 3-10. SB13 CPC Processing Calculations (Predicted Melter Feed Composition)

Case Number	**SB13Tk48-1**	**SB13Tk48-2**	**SB13Tk48-3**
Case Description	SB13 Sludge Only	SB13 Tk48 FBSR No SWPF	SB13 Tk48 FBSR SWPF
Weight % Total Solids	50.00%	50.00%	50.00%
Weight % Calcined Solids	36.82%	36.23%	36.45%
Slurry Density	1.420	1.420	1.420
Anions, mg/kg slurry			
Nitrite (mg/kg)	0	0	0
Nitrate (mg/kg)	15,183	43,522	44,110
Formate (mg/kg)	32,168	14,242	15,457
Sulfate (mg/kg)	284	282	268
Chloride (mg/kg)	12	12	12
Phosphate (mg/kg)	47	46	47
Oxalate (mg/kg)	0	0	942
Slurry TIC (mg/kg)	0	0	0
Coal/Carbon source, mg/kg slurry	0	9,130	9,232
Total Carbon, mg/kg slurry basis	8,582	12,929	13,356
Cations, wt % Calcined Solids			
Al	2.51	2.52	2.68
B	1.49	1.49	1.49
Ba	0.09	0.09	0.09
Ca	0.87	0.88	0.90
Ce	0.29	0.29	0.29
Cr	0.08	0.08	0.08
Cu	0.02	0.02	0.03
Fe	10.41	10.49	10.68
K	0.06	0.06	0.06
La	0.10	0.10	0.10
Li	2.23	2.23	2.23
Mg	0.12	0.12	0.13
Mn	1.81	1.83	1.82
Na	11.42	11.48	10.92
Ni	0.30	0.30	0.30
Pb	0.16	0.16	0.16
Si	22.02	22.03	22.09
S	0.02	0.02	0.02
Th	1.01	1.02	0.98
Ti	0.54	0.55	0.57
U	0.52	0.52	0.55
Zn	0.02	0.02	0.03
Zr	0.18	0.18	0.19

The above twelve processing cases (scenarios for each sludge batch) were evaluated using the SRNL Acid Calculation Spreadsheet. In each case, the acid mix was adjusted to produce a predicted melter feed REDOX of 0.20. In all cases there was more than enough formic acid to reduce all the mercury in the sludge and still produce a REDOX of 0.20. In other words, the CPC process could handle more coal than is present in the predicted sludge batches studied.

3.2.2 *Abnormal CPC Processing*

There are a number of process upsets that could significantly change the carbon concentration in the melter feed. A few examples of potential abnormal conditions include:

- The activity of the noble metals significantly impacts the formate destruction which impacts the melter feed formate concentration. Using SB11 as an example, the assumed values for nitrate conversion and formate destruction were adjusted to determine whether a 0.20 REDOX could be met with only the minimal formic acid required to reduce mercury.
- What would happen if oxalic acid cleaning of the SWPF actinide filters would lead to a 10x increase in oxalate in a single batch?
- What if a process upset in the FBSR increased the concentration of coal in the product by 50%?
- What if a process upset in the SWPF cesium process led to a 10x increase in organic in the strip effluent stream?

3.2.2.1 Low Formate Destruction

Formic acid is used for a number of reasons in DWPF processing, including neutralizing the sludge, destruction of nitrite and carbonate, reduction of mercury and manganese. An unwanted reaction of formic acid is the noble metal catalyzed decomposition of formic acid to hydrogen and carbon dioxide. Assuming no formate destruction in the SRAT or SME, enough formic acid is added to reduce Mn and Hg and produce a REDOX of 0.20. Results are summarized in Table 3-11.

3.2.2.2 High FBSR Coal Concentration

Carbon from coal is entrained in the FBSR product at an expected concentration of 15 % of the slurry solids. If processing problems led to a 50% increase in the entrained carbon, the acid mix would need to be adjusted to produce a predicted REDOX of 0.20. Note that the predicted REDOX can just barely be controlled with a 50% increase of carbon (22.5% total solids). However, there isn’t enough formic acid to reduce Hg and Mn present in the DWPF SRAT, a key CPC processing constraint necessary for stripping mercury. Results are summarized in Table 3-12.

3.2.2.3 High ARP Oxalate Concentration

The ARP oxalate contributes <0.01% of the carbon. Even a large increase of oxalate will have minimal impact on REDOX.

3.2.2.4 High Nitrate Destruction

In the baseline analysis, it was assumed that 2.6% of the nitrite was converted to nitrate. In experiments with minimal catalytic reduction of nitrate and nitrite to ammonia, a maximum of 33% of nitrite will be converted to nitrate (the rest will be converted to N_xO_y) and no nitrate is reduced to nitrite or ammonia. The nitrate concentration in the melter feed remains high and maximum formic acid can be added for REDOX control. In experiments with maximum catalytic reduction of nitrate and nitrite to ammonia, all of the nitrite is destroyed and a portion of the nitrate is reduced to ammonia. This leads to minimum nitrate concentration in the melter feed so less formic acid can be added to produce a REDOX of 0.20. A test case was completed assuming maximum catalytic activity to form ammonia and a -30% nitrite to nitrate conversion in the SRAT (all nitrate destroyed, no nitrate generation, 30% of nitrite reduced to ammonia) and 20% nitrate destruction in SME. Even under these extreme conditions, the acid mix can be adjusted to produce a predicted REDOX of 0.20. Results are summarized in Table 3-13.

3.2.2.5 High SWPF Organic Concentration

In the baseline study, it was assumed there was no organic in the SWPF cesium stream as the organic in the SWPF is very small compared to the coal in the FBSR. In addition, most of the organic is removed during boiling in the CPC, so very little organic will be present in the melter feed. Even if an SWPF process upset leads to much higher organic, the added carbon is still insignificant compared to the coal and formate.

3.2.2.6 High Coal, Oxalate, SWPF Organic Concentration

If more than one of these abnormal conditions happens concurrently, the amount of formic acid that can be added may be inadequate to control pH. In one simulation, the following parameters were at their extremes:

1. Low formate destruction (10%)
2. Low nitrate conversion (-30%)
3. High coal in FBSR (50% high)
4. High oxalate in Actinide stream (10x nominal)

If these conditions were used during processing of SB11, the final REDOX would be 0.29 for the case with without SWPF streams and 0.27 in the case with the SWPF streams. This means the final REDOX would be more reducing than targeted. Results are summarized in Table 3-14.

3.2.2.7 High Acid Stoichiometry

Processing in DWPF often requires more acid than is predicted to maximize the rate of nitrite destruction and mercury stripping. In runs with excessive acid, it can lead to high hydrogen generation. Typical processing is completed at approximately 120% of the minimum stoichiometry but might need to be increased as high as 150% of the minimum stoichiometry. A higher acid stoichiometry could achieve the REDOX target but will lead to two other issues. First, higher acid stoichiometry (i.e., higher total acid addition) produces more free formic acid in the CPC process, which will lead to higher hydrogen generation in the CPC and melter offgas system. Each sludge batch has its own concentration and activity of noble metals. Based on recent sludge batch processing, Koopman acid stoichiometry >150% is unlikely to be feasible in the CPC and will likely exceed the TOC limit in DWPF.

Higher acid stoichiometry leads to an increase in the amount of formic acid and nitric acid used. The formate concentration in the melter feed increases by 156% due to higher acid stoichiometry. A REDOX of 0.20 can be achieved; however the TOC concentration in the melter feed is approximately 17,500 mg/kg, approaching the current DWPF limit of 18500 mg/kg. Results are summarized in Table 3-15.

3.2.2.8 High Sludge Oxalate

Tank cleaning prior to closure uses oxalic acid to retrieve as much sludge as practical. Current planning is to destroy the oxalate prior to sludge washing. In case the oxalate destruction process is inadequate or delayed, a test was completed with 10,000 mg/kg oxalate in sludge assuming no oxalate destruction in the CPC processing. A REDOX of 0.20 can be achieved; however the formate concentration in the melter feed is approximately 18,000 mg/kg, approaching the current DWPF TOC limit of 18,500 mg/kg. Results are summarized in Table 3-16.

Table 3-11. SB11 High Formate CPC Processing Calculations (Predicted Melter Feed Composition)

Case Number	**SB11Tk48-4**	**SB11Tk48-5**	**SB11Tk48-6**
Case Description	SB11 Sludge Only	SB11 Tk48 FBSR No SWPF	SB11 Tk48 FBSR SWPF
Mass Carbon, g	0.00	30.38	30.32
Nitric Acid, M	0.240	0.773	0.835
Formic Acid, M	0.954	0.399	0.464
Formic Needed for Hg & Mn, M	0.182	0.168	0.191
SME Total Mass	3,449.76	3,462.35	3,420.91
Nitrite (mg/kg)	0	0	0
Nitrate (mg/kg)	20,014	44,824	45,421
Formate (mg/kg)	40,081	18,581	19,933
Sulfate (mg/kg)	286	287	273
Chloride (mg/kg)	12	12	13
Phosphate (mg/kg)	47	47	48
Oxalate (mg/kg)	0	0	943
Slurry TIC (treated as carbonate) mg/kg	0	0	0
Coal/Carbon source, mg/kg slurry basis	0	8,773	8,863
Total Carbon, mg/kg slurry basis	10,694	13,731	14,181
Cations, wt % Calcined Solids Basis			
Al	2.51	2.52	2.68
B	1.49	1.49	1.49
Ba	0.09	0.09	0.09
Ca	0.88	0.88	0.90
Ce	0.29	0.29	0.29
Cr	0.08	0.08	0.08
Cu	0.02	0.02	0.03
Fe	10.41	10.47	10.67
K	0.06	0.06	0.06
La	0.10	0.10	0.10
Li	2.23	2.23	2.23
Mg	0.12	0.12	0.13
Mn	1.81	1.82	1.82
Na	11.42	11.47	10.91
Ni	0.30	0.30	0.30
Pb	0.16	0.16	0.16
Si	22.02	22.03	22.09
S	0.02	0.02	0.02
Th	1.01	1.02	0.98
Ti	0.54	0.55	0.56
U	0.52	0.52	0.54
Zn	0.02	0.02	0.03
Zr	0.18	0.18	0.19

Table 3-12. SB11 High Coal CPC Processing Calculations (Predicted Melter Feed Composition)

Case Number	**SB11Tk48-7**	**SB11Tk48-8**	**SB11Tk48-9**
Case Description	SB11 Sludge Only	SB11 Tk48 FBSR No SWPF	SB11 Tk48 FBSR SWPF
Predicted Redox, $Fe^{+2}/\Sigma Fe$	0.200	0.200	0.200
Mass Carbon, g	0.00	53.16	53.06
Nitric Acid, M	0.144	1.163	1.252
Formic Acid, M	1.051	0.010	0.046
Formic Needed for Hg & Mn, M	0.182	0.168	0.191
SME Total Mass	3,376.11	3,501.72	3,457.93
Nitrite (mg/kg)	0	0	0
Nitrate (mg/kg)	15,789	62,681	63,358
Formate (mg/kg)	32,563	2,890	3,818
Sulfate (mg/kg)	293	284	270
Chloride (mg/kg)	12	12	12
Phosphate (mg/kg)	48	47	47
Oxalate (mg/kg)	0	0	1
Slurry TIC (treated as carbonate) mg/kg	0	0	0
Coal/Carbon source, mg/kg slurry basis	0	15,181	15,344
Total Carbon, mg/kg slurry basis	8,688	15,952	16,363
Cations, wt % Calcined Solids Basis			
Al	2.51	2.52	2.68
B	1.49	1.49	1.49
Ba	0.09	0.09	0.09
Ca	0.88	0.88	0.90
Ce	0.29	0.29	0.29
Cr	0.08	0.08	0.08
Cu	0.02	0.02	0.03
Fe	10.41	10.47	10.67
K	0.06	0.06	0.06
La	0.10	0.10	0.10
Li	2.23	2.23	2.23
Mg	0.12	0.12	0.13
Mn	1.81	1.82	1.82
Na	11.42	11.47	10.91
Ni	0.30	0.30	0.30
Pb	0.16	0.16	0.16
Si	22.02	22.03	22.09
S	0.02	0.02	0.02
Th	1.01	1.02	0.98
Ti	0.54	0.55	0.56
U	0.52	0.52	0.54
Zn	0.02	0.02	0.03
Zr	0.18	0.18	0.19

Table 3-13. SB11 Low Nitrate CPC Processing Calculations (Predicted Melter Feed Composition)

Case Number	**SB11Tk48-10**	**SB11Tk48-11**	**SB11Tk48-12**
Case Description	SB11 Sludge Only	SB11 Tk48 FBSR No SWPF	SB11 Tk48 FBSR SWPF
Mass Carbon, g	0.00	30.38	30.32
Nitric Acid, M	0.248	0.872	0.933
Formic Acid, M	0.946	0.301	0.366
Formic Needed for Hg & Mn, M	0.182	0.168	0.191
SME Total Mass	3,393.05	3,453.89	3,409.46
Nitrite (mg/kg)	0	0	0
Nitrate (mg/kg)	14,090	40,794	41,255
Formate (mg/kg)	29,449	11,117	12,275
Sulfate (mg/kg)	291	288	274
Chloride (mg/kg)	12	12	13
Phosphate (mg/kg)	48	47	48
Oxalate (mg/kg)	0	0	1
Slurry TIC (treated as carbonate) mg/kg	0	0	0
Coal/Carbon source, mg/kg slurry basis	0	8,795	8,892
Total Carbon, mg/kg slurry basis	7,857	11,761	12,168
Cations, wt % Calcined Solids Basis			
Al	2.51	2.52	2.68
B	1.49	1.49	1.49
Ba	0.09	0.09	0.09
Ca	0.88	0.88	0.90
Ce	0.29	0.29	0.29
Cr	0.08	0.08	0.08
Cu	0.02	0.02	0.03
Fe	10.41	10.47	10.67
K	0.06	0.06	0.06
La	0.10	0.10	0.10
Li	2.23	2.23	2.23
Mg	0.12	0.12	0.13
Mn	1.81	1.82	1.82
Na	11.42	11.47	10.91
Ni	0.30	0.30	0.30
Pb	0.16	0.16	0.16
Si	22.02	22.03	22.09
S	0.02	0.02	0.02
Th	1.01	1.02	0.98
Ti	0.54	0.55	0.56
U	0.52	0.52	0.54
Zn	0.02	0.02	0.03
Zr	0.18	0.18	0.19

Table 3-14. SB11 All Extreme CPC Processing Calculations (Predicted Melter Feed Composition)

Case Number	SB11Tk48-13	SB11Tk48-14	SB11Tk48-15
Case Description	SB11 Sludge Only	SB11 Tk48 FBSR No SWPF	SB11 Tk48 FBSR SWPF
Predicted Redox, $Fe^{+2}/\Sigma Fe$	0.200	0.491	0.471
Mass Carbon, g	0.00	53.16	53.06
Nitric Acid, M	0.311	1.005	1.108
Formic Acid, M	0.883	0.168	0.191
Formic Needed for Hg & Mn, M	0.182	0.168	0.191
SME Total Mass	3,432.73	3,481.48	3,441.89
Nitrite (mg/kg)	0	0	0
Nitrate (mg/kg)	16,668	46,226	47,893
Formate (mg/kg)	34,024	8,765	9,152
Sulfate (mg/kg)	288	285	271
Chloride (mg/kg)	12	12	12
Phosphate (mg/kg)	47	47	48
Oxalate (mg/kg)	0	0	11
Slurry TIC (treated as carbonate) mg/kg	0	0	0
Coal/Carbon source, mg/kg slurry basis	0	15,269	15,415
Total Carbon, mg/kg slurry basis	9,078	17,607	17,860
Cations, wt % Calcined Solids Basis			
Al	2.51	2.52	2.68
B	1.49	1.49	1.49
Ba	0.09	0.09	0.09
Ca	0.88	0.88	0.90
Ce	0.29	0.29	0.29
Cr	0.08	0.08	0.08
Cu	0.02	0.02	0.03
Fe	10.41	10.47	10.67
K	0.06	0.06	0.06
La	0.10	0.10	0.10
Li	2.23	2.23	2.23
Mg	0.12	0.12	0.13
Mn	1.81	1.82	1.82
Na	11.42	11.47	10.91
Ni	0.30	0.30	0.30
Pb	0.16	0.16	0.16
Si	22.02	22.03	22.09
S	0.02	0.02	0.02
Th	1.01	1.02	0.98
Ti	0.54	0.55	0.56
U	0.52	0.52	0.54
Zn	0.02	0.02	0.03
Zr	0.18	0.18	0.19

Table 3-15. SB10 High Acid Stoichiometry CPC Processing Calculations (Predicted Melter Feed Composition)

Case Number	SB10Tk48-4	SB10Tk48-5	SB10Tk48-6
Case Description	SB10 Sludge Only	SB10 Tk48 FBSR No SWPF	SB10 Tk48 FBSR SWPF
Mass Carbon, g	0.00	26.16	26.14
Nitric Acid, M	0.327	0.776	0.829
Formic Acid, M	1.625	1.140	1.233
Formic Needed for Hg & Mn, M	0.230	0.215	0.233
SME Total Mass	3,512.20	3,555.72	3,513.16
Nitrite (mg/kg)	0	0	0
Nitrate (mg/kg)	24,295	46,823	47,132
Formate (mg/kg)	52,931	37,473	37,850
Sulfate (mg/kg)	312	307	291
Chloride (mg/kg)	13	13	13
Phosphate (mg/kg)	51	51	51
Oxalate (mg/kg)	0	0	1
Slurry TIC (treated as carbonate) mg/kg	0	0	0
Coal/Carbon source, mg/kg slurry basis	0	7,358	7,441
Total Carbon, mg/kg slurry basis	14,122	17,356	17,539
Cations, wt % Calcined Solids Basis			
Al	2.51	2.50	2.66
B	1.49	1.49	1.49
Ba	0.09	0.09	0.09
Ca	0.88	0.87	0.89
Ce	0.29	0.29	0.29
Cr	0.08	0.08	0.08
Cu	0.02	0.02	0.03
Fe	10.42	10.39	10.58
K	0.06	0.06	0.06
La	0.10	0.10	0.10
Li	2.23	2.23	2.23
Mg	0.12	0.12	0.13
Mn	1.81	1.81	1.80
Na	11.43	11.40	10.85
Ni	0.30	0.30	0.30
Pb	0.16	0.15	0.15
Si	22.02	22.02	22.08
S	0.02	0.02	0.02
Th	1.01	1.01	0.97
Ti	0.55	0.54	0.56
U	0.52	0.52	0.54
Zn	0.02	0.02	0.03
Zr	0.18	0.18	0.19

Table 3-16. SB10 High Sludge Oxalate CPC Processing Calculations (Predicted Melter Feed Composition)

Case Number	SB10Tk48-4	SB10Tk48-5	SB10Tk48-6
Case Description	SB10 Sludge Only	SB10 Tk48 FBSR No SWPF	SB10 Tk48 FBSR SWPF
Mass Carbon, g	0.00	29.21	29.49
Nitric Acid, M	0.410	0.909	0.973
Formic Acid, M	1.521	0.983	1.068
Formic Needed for Hg & Mn, M	0.230	0.215	0.233
SME Total Mass	3,517.33	3,576.37	3,535.85
Nitrite (mg/kg)	0	0	0
Nitrate (mg/kg)	28,559	53,398	53,722
Formate (mg/kg)	49,617	32,488	32,909
Sulfate (mg/kg)	311	305	289
Chloride (mg/kg)	13	13	13
Phosphate (mg/kg)	51	50	51
Oxalate (mg/kg)	3,069	2,960	2,795
Slurry TIC (treated as carbonate) mg/kg	0	0	0
Coal/Carbon source, mg/kg slurry basis	0	8,168	8,339
Total Carbon, mg/kg slurry basis	14,076	17,644	17,882
Cations, wt % Calcined Solids Basis			
Al	2.51	2.50	2.66
B	1.49	1.49	1.49
Ba	0.09	0.09	0.09
Ca	0.88	0.87	0.90
Ce	0.29	0.29	0.29
Cr	0.08	0.08	0.08
Cu	0.02	0.02	0.03
Fe	10.43	10.40	10.59
K	0.06	0.06	0.06
La	0.10	0.10	0.10
Li	2.23	2.23	2.23
Mg	0.12	0.12	0.13
Mn	1.82	1.81	1.81
Na	11.44	11.42	10.86
Ni	0.30	0.30	0.30
Pb	0.16	0.15	0.15
Si	22.02	22.02	22.09
S	0.02	0.02	0.02
Th	1.01	1.01	0.97
Ti	0.55	0.54	0.56
U	0.52	0.52	0.54
Zn	0.02	0.02	0.03
Zr	0.18	0.18	0.19

3.3 DWPF Melter Off-Gas Flammability Assessment

Melter off-gas flammability is determined largely by: (1) total organic carbon (TOC) in the feed, (2) feed rate, (3) air purges for combustion and cooling, (4) melter vapor space temperature, and (5) off-gas surge. In essence, all these variables are controlled either by the choice of flowsheet or by the mode of operation, and their impact on off-gas flammability is highly interdependent. For example, when TOC is increased at fixed air flows, the melter vapor space temperature would have to be increased in order to burn excess carbon. The melter vapor space temperature can be increased by reducing the feed rate, thereby exposing a greater area of melt surface for increased radiation shine into the vapor space. Reduced feed rate in turn not only reduces the rate of TOC fed to the melter but decreases the likelihood of off-gas surging as well.

Two computer models have been used to describe these complex interdependencies quantitatively and further set the operating limits of these variables in the form of feed interlocks and technical safety requirements (TSR).[10, 11] The first model, called the 4-stage cold cap model, describes the chemistry of cold cap reactions thermodynamically and predicts the compositions of both glass and calcine gases from a given feed composition. The composition of calcine gases is then used as the input to the second model, called the off-gas dynamics model, which predicts the transient behavior of the DWPF melter off-gas system, including the potential for off-gas flammability, for various upset scenarios. The baseline upset scenario used in the off-gas flammability assessment is the design basis 3X off-gas surge, which is defined later in this section.

The following theoretical limits have been established for SB6 in order to ensure full compliance with the off-gas flammability safety bases for both normal and seismic operations:[12]

- TOC ≤18,900 ppm.
- Feed rate ≤1.5 GPM
- Total melter air purge (FIC3221A) ≥ 900 lb/hr (nominally at 1,070 lb/hr)
- Backup film cooler air purge (FIC3221B) ≥233 lb/hr (nominally at 340 lb/hr)
- Melter vapor space temperature (TI4085D) ≥ 460 °C

The actual TSR and feed interlock limits used in the field are to be set by applying appropriate analytical or instrument uncertainties to these theoretical limits.

Of all those variables affecting the off-gas flammability, the focus of this assessment is on TOC, particularly on determining the maximum amount of coal that can be fed to the DWPF melter without exceeding the off-gas flammability safety basis limits. Since SB10 was found to be the worst-case batch in terms of meeting the CPC processing targets, assessment was made using SB10 as the baseline feed. Specifically, of the nine SB10 cases for which the acid calculations were performed, the following three cases were chosen: (1) sludge-only at 100% stoichiometric acid addition (SB10Tk48-1), (2) sludge-only at 150% stoichiometric acid addition (SB10Tk48-4), and (3) sludge/Tank 48/SWPF blend at 150% stoichiometric acid addition (SB10Tk48-6). Hence, the impact of increased acid addition on off-gas flammability was assessed by comparing Cases 1 and 2, and that of Tank 48 and SWPF feeds by comparing Cases 2 and 3. In all cases, the target redox was 0.2, while the target waste loading in glass was 40%. Three additional cases were also considered by adding coal to each of the three feeds without performing the acid calculations.

3.3.1 *Cold Cap Model Input*

The feed data for the three cases chosen are shown in Table 3-17. TOC is increased by 33% from 10,646 to 14,122 ppm when acid addition was increased from 100% to 150% stoichiometry. It is also noted that since no oxalate is present in the assumed composition of SB10, 100% of the TOC for Cases 2 and 3 is solely due to the formic acid addition. TOC is further increased by 24% from 14,122 to 17,539 ppm by adding Tank 48 coal and SWPF streams in Case 3. Since the impact of SWPF streams on TOC was shown to be minimal,[12] much of this increase in TOC is due to the addition of Tank 48 coal. However, the amount of coal added at 7,441 ppm is clearly more than twice the difference in TOC between Cases 2 and 3. This is because coal, which is assumed to be 100% carbon, also acts as a reducing agent in the current redox control scheme and, therefore, much less formic acid than in Case 2 is added in order to prevent the feed from becoming too reducing despite the fact that the acid addition was the same at 150% stoichiometry in both cases.

The feed data shown in Table 3-17 were charge balanced next in order to convert them into a neutral species form, as required by the 4-stage cold cap model, and the resulting melter feed compositions are shown in Tables B-1 to B-3. The charge balance results were excellent for the Case 2 feed (SB10Tk48-4); the calculated insoluble fraction of Na in the feed matched that due to frit well. However, for Cases 2 and 3 (SB10Tk48-4 and SB10Tk48-6), the charge balance was off by 36% and -16%, respectively. It is also noted that these feed compositions are based on the current DWPF maximum feed rate of 1.5 GPM at the assumed specific gravity of 1.42.

The feed compositions given in Tables B-1, B-2, and B-3 were further decomposed into the final input form for the 4-stage cold cap model, as shown in Table 3-18, Table 3-19, and Table 3-20, respectively. As described elsewhere,[10] the model approximates the complex melting process as a continuous, 4-stage countercurrent equilibrium reactor, and the temperature of each stage is set progressively higher from the top (Stage 1) to bottom stage (Stage 4). The non ideality that exists among various melt phases that form is partially accounted for in lower stages with the use of the Gibbs free energy database for the complex liquids, which was developed at the National Institute of Standards and Technology (NIST).[13] In forming these model input vectors, all salts except sulfates were pre-decomposed into oxides and corresponding gases as follows:

$$2\,Fe(OH)_3 \;=\; Fe_2O_3 + 3\,H_2O \tag{2}$$

$$2\,NaCOOH \;=\; Na_2C_2O_4 + H_2 \tag{3}$$

$$Na_2C_2O_4 = Na_2O + CO + CO_2 \tag{4}$$

$$2\,NaNO_3 \;=\; 2\;NaNO2 + O2 \tag{5}$$

$$2\,NaNO2 = Na_2O + NO + NO_2 \tag{6}$$

In particular, the decomposition of sodium nitrate is known to begin with the release of oxygen, thereby converting to nitrite at low temperatures, e.g., ~350°C, and the subsequent decomposition of nitrite, which can take several different routes depending on the presence or absence of air and other gases, can persist beyond 850 °C. Based on this ample experimental evidence, the model assumes that the decomposition of nitrite shown in Eq. (6) occurs over a much wider temperature range compared to other calcine reactions at ~30:50:20 split among Stage 1 to 3, respectively. Likewise, coal was also assumed to react over a wide temperature range, and the input vector shown in Table 3-20 reflects a 30:50:20 split of coal among Stages 1 to 3, respectively.

Table 3-17. SB10 Feed Data Used for Melter Off-Gas Flammability Assessment.

Case Number	1	2	3
Feed Number	SB10Tk48-1	SB10Tk48-4	SB10Tk48-6
Feed Makeup	Sludge Only	Sludge Only	Sludge Tk48 FBSR SWPF
FBSR (g/g sludge)	0	0	0.09
ARP (g/g sludge)	0	0	0.14
MCU (g/g sludge)	0	0	0.61
Coal/Carbon source, mg/kg slurry	0	0	7,441
Acid Addition (% Stoichiometry)	100	150	150
Total Solids (wt%)	50	50	50
Calcined Solids (wt%)	37.84	35.82	35.54
Slurry Density (g/ml)	1.420	1.420	1.420
Anions, mg/kg slurry			
Nitrate (mg/kg)	16,703	24,295	47,132
Formate (mg/kg)	39,901	52,931	37,850
Sulfate (mg/kg)	329	312	291
Chloride (mg/kg)	14	13	13
Phosphate (mg/kg)	54	51	51
Oxalate (mg/kg)	0	0	1
Total Carbon, mg/kg slurry	10,646	14,122	17,539
Cations, wt % Calcined Solids			
Al	2.51	2.51	2.66
B	1.49	1.49	1.49
Ba	0.09	0.09	0.09
Ca	0.88	0.88	0.89
Ce	0.29	0.29	0.29
Cr	0.08	0.08	0.08
Cu	0.02	0.02	0.03
Fe	10.42	10.42	10.58
K	0.06	0.06	0.06
La	0.10	0.10	0.10
Li	2.23	2.23	2.23
Mg	0.12	0.12	0.13
Mn	1.81	1.81	1.80
Na	11.43	11.43	10.85
Ni	0.30	0.30	0.30
Pb	0.16	0.16	0.15
Si	22.02	22.02	22.08
S	0.02	0.02	0.02
Th	1.01	1.01	0.97
Ti	0.55	0.55	0.56
U	0.52	0.52	0.54
Zn	0.02	0.02	0.03
Zr	0.18	0.18	0.19

Table 3-18. 4-Stage Cold Cap Model Input for Case 1 (SB10Tk48-1) at 1.5 GPM.

Species	Stage 1 (gmole/hr)	Stage 2 (gmole/hr)	Stage 3 (gmole/hr)
Al2O3	0	95.812	0
B2O3	142.218	0	0
CaO	0	44.408	0
CuO	0.775	0	0
Fe2O3	192.338	0	0
K2O	1.574	0	0
Li2O	0	331.343	0
MgO	0	0	10.465
MnO2	0	6.811	0
MnO	61.301	0	0
Na2O	223.844	286.767	0
NiO	10.623	0	0
SiO2	1617.102	0	0
CaSO4	0	0	0.63668
Na2SO4	0	0	1.869
H2O	532.665	0	0
CO	0	241.668	0
CO2	0	241.668	0
H2	241.367	0	0
O2	19.825	39.518	14.685
NO	19.825	38.916	14.685
NO2	19.825	38.916	14.685

Table 3-19. 4-Stage Cold Cap Model Input for Case 2 (SB10Tk48-4) at 1.5 GPM.

Species	Stage 1 (gmole/hr)	Stage 2 (gmole/hr)	Stage 3 (gmole/hr)
Al2O3	0	91.435	0
B2O3	135.721	0	0
CaO	0	42.383	0
CuO	0.739	0	0
Fe2O3	183.552	0	0
K2O	1.502	0	0
Li2O	0	316.207	0
MgO	0	0	9.987
MnO2	0	6.500	0
MnO	58.501	0	0
Na2O	343.808	143.478	0
NiO	10.138	0	0
SiO2	1543.232	0	0
CaSO4	0	0	0.604189
Na2SO4	0	0	1.783
H2O	508.336	0	0
CO	0	323.212	0
CO2	0	323.212	0
H2	322.925	0	0
O2	39.840	46.876	21.535
NO	39.840	46.301	21.535
NO2	39.840	46.301	21.535

Table 3-20. 4-Stage Cold Cap Model Input for Case 3 (SB10Tk48-6) at 1.5 GPM.

Species	Stage 1 (gmole/hr)	Stage 2 (gmole/hr)	Stage 3 (gmole/hr)
Al2O3	0	93.614	0
B2O3	131.076	0	0
CaO	0	39.101	0
CuO	0.752	0	0
Fe2O3	180.049	0	0
K2O	1.344	0	0
Li2O	0	305.384	0
MgO	0	0	9.788
MnO2	0	6.244	0
MnO	56.196	0	0
Na2O	344.006	102.744	0
NiO	9.624	0	0
SiO2	1494.571	0	0
CaSO4	0	0	3.322188
Na2SO4	0	0	1.620
coal	90.095	150.159	60.06365
H2O	507.621	0	0
CO	0	224.931	0
CO2	0	224.931	0
H2	224.636	0	0
O2	75.215	87.988	40.657
NO	75.215	87.412	40.657
NO2	75.215	87.412	40.657

3.3.2 *Cold Cap Model Results*

The compositions of both calcine gases and glasses predicted by the cold cap model are shown in Table 3-21 and Table 3-22, respectively, for the three SB10 cases considered. It is noted in Table 3-21 that the calculated TOC's became 6-13% higher than those given in Table 3-17 after the charge balance. More importantly, however, it is surprising to see that the molar ratios of CO/CO_2 and $H_2/(CO+CO_2)$ become lower as the TOC increases, which means that the melter off-gas would become less flammable with increasing TOC. This seemingly-counterintuitive trend can only occur when more oxygen becomes available with increasing TOC to burn off excess carbon in the cold cap. And the increased availability of oxygen with increasing TOC is a direct result of the current acid addition scheme.

For example, when increased acid addition is called for in Case 2 at 150% stoichiometry over that of Case 1, the acid calculation requires that the total acid addition be partitioned at a higher nitric-to-formic ratio in order to target the same redox ratio of 0.2, as shown by Eq. (1). As a result, the nitrate level in the Case 2 feed (SB10Tk48-4) was 45% higher than that of Case 1 (SB10Tk48-1), while the formate level was increased by 33%. Since the nitrate is the primary source of oxygen in the cold cap via Reactions (5) and (6), more oxygen was available per mole of carbon in Case 2 than in Case 1, resulting in lower molar ratios of CO/CO_2 and $H_2/(CO+CO_2)$.

Table 3-21. Calcine Gas Compositions Calculated by 4-Stage Cold Cap Model at 1.5 GPM.

Case	1	2	3
Calcine Gases	SB10Tk48-1 (gmole/hr)	SB10Tk48-4 (gmole/hr)	SB10Tk48-6 (gmole/hr)
H2O	707.9800	773.1496	741.066
CO2	456.9599	617.4779	717.876
H2	66.0253	58.1861	14.424
N2	73.4218	107.6854	203.294
CO	26.4689	28.8632	9.248
O2	0.0000	0.0000	0.000
SO2	0.0064	0.0092	0.043
NO	0.0000	0.0000	0.000
NO2	0.0000	0.0000	0.000
NaBO2 g	0.0004	0.0004	0.001
Total	1,330.8628	1,585.3718	1,685.9518
Calculated TOC (ppm)	11,962	15,999	18,575
CO/CO2	0.058	0.047	0.013
H2/(CO+CO2)	0.137	0.090	0.020
Required Combustion Air (lb/hr)	53	49	13

Table 3-22. Glass Compositions Calculated by 4-Stage Cold Cap Model at 1.5 GPM.

Phases	SB10Tk48-1 (gmole/hr)	SB10Tk48-4 (gmole/hr)	SB10Tk48-6 (gmole/hr)
Melt			
SiO2 l	1,077.107	1,027.927	1,021.863
Na2SiO3	512.421	489.013	448.460
LiBO2 l	284.062	271.086	261.816
LiAlO2 l	191.617	182.863	187.303
Fe3O4 l	61.299	57.798	39.060
MgSiO3 l	8.989	8.578	8.492
FeO l	13.198	12.444	8.410
CaFe2O4	12.177	11.617	10.759
B2O3 l	0.000	0.000	0.000
Ca2SiO4	13.067	12.472	11.523
Ca3MgSi2	1.413	1.349	1.239
Fe2SiO4	1.196	1.115	0.548
KBO2	0.331	89.154	80.750
Li2O l	93.421	1.344	1.195
K2SiO3	1.408	0.316	0.297
Spinel			
NiFe2O4	10.624	10.139	9.624
Mn3O4	22.699	21.668	20.813
CuFe2O4	0.776	0.740	0.752
MgFe2O4	0.062	0.059	0.057
ICP			
Fe2O3	68.973	66.978	95.507
NiO	0	0.000	4.896
CaSO4	2.501	2.384	4.896
Calculated Fe(+2)/Fe(total) =	0.20	0.20	0.13

The relative increase in nitrate level becomes even greater when 7,441 ppm of coal is added at 150% stoichiometric acid addition in Case 3. This is because coal, which is assumed to be 100% carbon, acts as a stronger reducing agent than formate in the current redox control scheme, which is reflected by twice as large a coefficient for coal as that for formate, as shown in Eq. (1). Therefore, in order to prevent the feed from becoming too reducing at such a large coal level, the total acid addition is partitioned at an even higher nitric-to-formic ratio in order to target the same redox ratio of 0.2. The resulting nitrate level in Case 3 (SB10Tk48-6) is nearly twice that of Case 2 (SB10Tk48-4), while the formate level is actually reduced in order to compensate for the coal addition. With such a large additional input of oxidant (nitrate), the molar ratios of CO/CO_2 and $H_2/(CO+CO_2)$ become much lower in Case 3 than in Case 2.

By contrast, the existing method of determining the maximum TOC limit is by increasing the concentrations of all formate salts in the baseline feed by the same ratio until the peak flammable gas concentration during the design basis 3X off-gas surge equals 60% of the lower flammability limit (LFL) without giving any consideration to the redox requirement. As a result, the calculated redox of such a maximum-TOC feed would become much higher than that of the baseline feed, and the resulting calcine gases much more flammable. This approach of increasing the formate level without the accompanying increase in nitrate level has been in use to simulate the situation where slugs of insoluble carbon species such as high-boiling aromatic compounds from the old precipitate hydrolysis process enter the melter. However, this scenario does not seem plausible if the formate carbon makes up much of TOC, since formate salts are highly soluble and therefore not likely to segregate. This makes the existing method of off-gas flammability assessment more conservative.

However, the current approach of selectively increasing the reductant level only seem relevant if coal makes up a significant portion of TOC, as in Case 3, since coal is insoluble and difficult to measure and the probability of its segregation is higher. In order to assess the impact of such a scenario of forming slugs of coal, an additional case (Case 4) was added to the scope where coal was added to the Case 2 feed, while ignoring the requirement that the target redox be maintained, until the final TOC equaled the current limit of 18,900. The compositions of calcine gases and glass thus calculated for Case 4 are compared in Table 3-23 and Table 3-24, respectively, against those of Case 3. It is clearly seen that the calculated molar ratios of CO/CO_2 and $H_2/(CO+CO_2)$ for Case 4 are an order of magnitude higher than their counterparts for Case 3, despite the fact that the maximum coal that can be added to the Case 4 feed without exceeding the current TOC limit is 2,948 ppm, which amounts to only 40% of that in the Case 3 feed. These results confirm that adding excess carbon above that of the baseline feed while ignoring the redox requirement results in a substantial increase in the CO and H_2 concentrations in the calcine gases.

The predicted SB10 glass oxides are split in groups or phases in Table 3-22 and Table 3-24. The letter **l** after each species in the melt phase denotes "liquid." These liquid or melt species were taken from the NIST database;[13] they do not necessarily represent independent molecular or ionic species but serve to represent the local associative order. Due to structural similarities, the spinels readily form solid solutions with one another and thus are assumed to form a separate phase of their own. On the other hand, each species included in the Invariant Condensed Phase (ICP) is assumed to form a separate phase by itself. Therefore, as more species are included in the ICP, the total number of phases to be considered in the equilibrium calculations increases, thus making it more difficult to achieve convergence. As expected, it is seen in Table 3-24 that adding excess carbon in the form of coal above that of the baseline feed while ignoring the redox requirement would make glass very reducing by pushing the glass redox ratio substantially above the current DWPF upper limit of 0.33. It is, however, noted that despite the high redox ratio the model did not predict formation of sulfides such as Ni_3S_2.

Table 3-23. Comparison of Calcine Gas Compositions for Cases 3 and 4.

Case	3	4
Calcine Gases	SB10Tk48-6 (gmole/hr)	SB10Tk48-4-maxCOAL (gmole/hr)
H2O	741.0655	676.9717
CO2	717.8761	670.4824
H2	14.4242	153.2888
N2	203.2940	107.5555
CO	9.2484	94.2967
O2	0.0000	0.0000
SO2	0.0431	0.0036
NO	0.0000	0.0000
NO2	0.0000	0.0000
NaBO2 g	0.0005	0.0004
Total	1685.9518	1702.5991
Calculated TOC (ppm)	18,575	18,900
CO/CO2	0.013	0.141
H2/(CO+CO2)	0.020	0.200
Req'd Combustion Air (lb/hr)	13	141

Table 3-24. Comparison of Glass Compositions for Cases 3 and 4.

Phases	SB10Tk48-6 (gmole/hr)	SB10Tk48-4-maxCOAL (gmole/hr)
Melt		
SiO2 l	1021.863	1005.599
Na2SiO3	448.460	488.380
LiBO2 l	261.816	270.728
LiAlO2 l	187.303	182.627
Fe3O4 l	39.060	88.717
MgSiO3 l	8.492	8.244
FeO l	8.410	53.211
CaFe2O4	10.759	4.800
B2O3 l	0.000	0.000
Ca2SiO4	11.523	15.282
Ca3MgSi2	1.239	1.729
Fe2SiO4	0.548	18.848
KBO2	80.750	0.323
Li2O l	1.195	89.042
K2SiO3	0.297	1.338
Spinel		
NiFe2O4	9.624	0.000
Mn3O4	20.813	0.000
CuFe2O4	0.752	0.000
MgFe2O4	0.057	0.000
ICP		
Fe2O3	95.507	0.000
NiO	4.896	10.125
CaSO4	4.896	2.386
MnO	0.000	64.921
Calculated Fe(+2)/Fe(total) =	0.13	0.49

3.3.3 *Off-Gas Dynamics Model Input*

The calculated calcine gas compositions for Cases 1 to 4 given in Table 3-21 and Table 3-23 were next used as the input to the off-gas dynamics model in order to check if the off-gas flammability safety basis limit of 60% of the LFL for normal operation is exceeded. Briefly, the model predicts the time-dependent responses of both the primary and backup DWPF melter off-gas systems under a variety of upset conditions.[10] It calculates 5-component mass and energy balances for the condensable and non condensable gases from first principles. It simulates all major DWPF melter off-gas system hardware, including 22 Proportional-Integral (PI) controllers and 26 valves, and the Distributed Control System (DCS) software logic to provide protection against extreme pressure transients and other operational anomalies such as equipment malfunction. It employs a 2-step global reaction scheme using the empirical first-order oxidation kinetics of CO and H_2 to model combustion of calcine gases in the melter vapor space.[12]

At the onset of 3X off-gas surge, the melter vapor space temperature (TI4085D) and the air purges are maintained at their respective minimum interlock values given earlier. The design basis 3X off-gas surge is assumed to proceed as follows:

- At time zero, the flow rates of both steam and non condensable gases increase 3-fold instantly and then immediately start to decrease linearly to 1.5 times (1.5X) the normal values during the first 1 minute.
- The flow rates of both steam and non condensable gases further decrease linearly to the normal values (1X) during the next 7 minutes.

3.3.4 *Results of Off-Gas Dynamics Model Runs*

Typical results of 3X off-gas surge simulation are shown in Figure 1 and Figure 2 for Cases 1 and 2, respectively, for normal operation. Each figure shows the transient profiles of the calcine gas flow into the melter vapor space, melter pressure, melter vapor space gas temperature and the concentration of flammable gases in the Off-Gas Condensate Tank (OGCT) in terms of percent of the lower flammability limit (LFL) during the first 2 and 1/2 minutes into the 3X surge. The peak concentrations of flammable gases read off from these figures are summarized in Table 3-25 along with key input variables. Since the molar ratios of CO/CO_2 and $H_2/(CO+CO_2)$ in the calcine gases decrease with increasing TOC at a fixed redox, the peak concentration of flammable gases is also shown to decrease, as the TOC increases from Case 1 to Case 3. This is because under the current acid addition scheme the rate of increase in nitrate level becomes higher with increasing

Table 3-25. Calculated Peak Concentrations of SB10 Flammable Gases @ OGCT during 3X Surge at 1.5 GPM.

Case	Feed	Acid Addition (% Stoich)	Coal (ppm)	TOC (ppm)	NO3 (ppm)	0.2 Redox Control?	Peak (% LFL)
1	SB10Tk48-1	100	0	11,962	18,799	Yes	17
2	SB10Tk48-4	150	0	15,999	27,568	Yes	15
3	SB10Tk48-6	150	7,441	18,575	52,047	Yes	4
4	SB10Tk48-4T	150	2,948	18,900	27,487	No	40
5	SB10Tk48-4C	150	5,063	20,900	27,289	No	60

6	SB10Tk48-1C	100	5,099	17,000	18,703	No	59

Figure 1. Results of 3X Off-Gas Surge Simulation for Normal Operation with Case 1 Feed (SB10Tk48-1: 100% Acid Stoichiometry, 11,962 ppm TOC, 1.5 GPM Feed Rate; TI4085D = 460 °C; FIC3221A = 900 PPH; FIC3221B = 233 PPH).

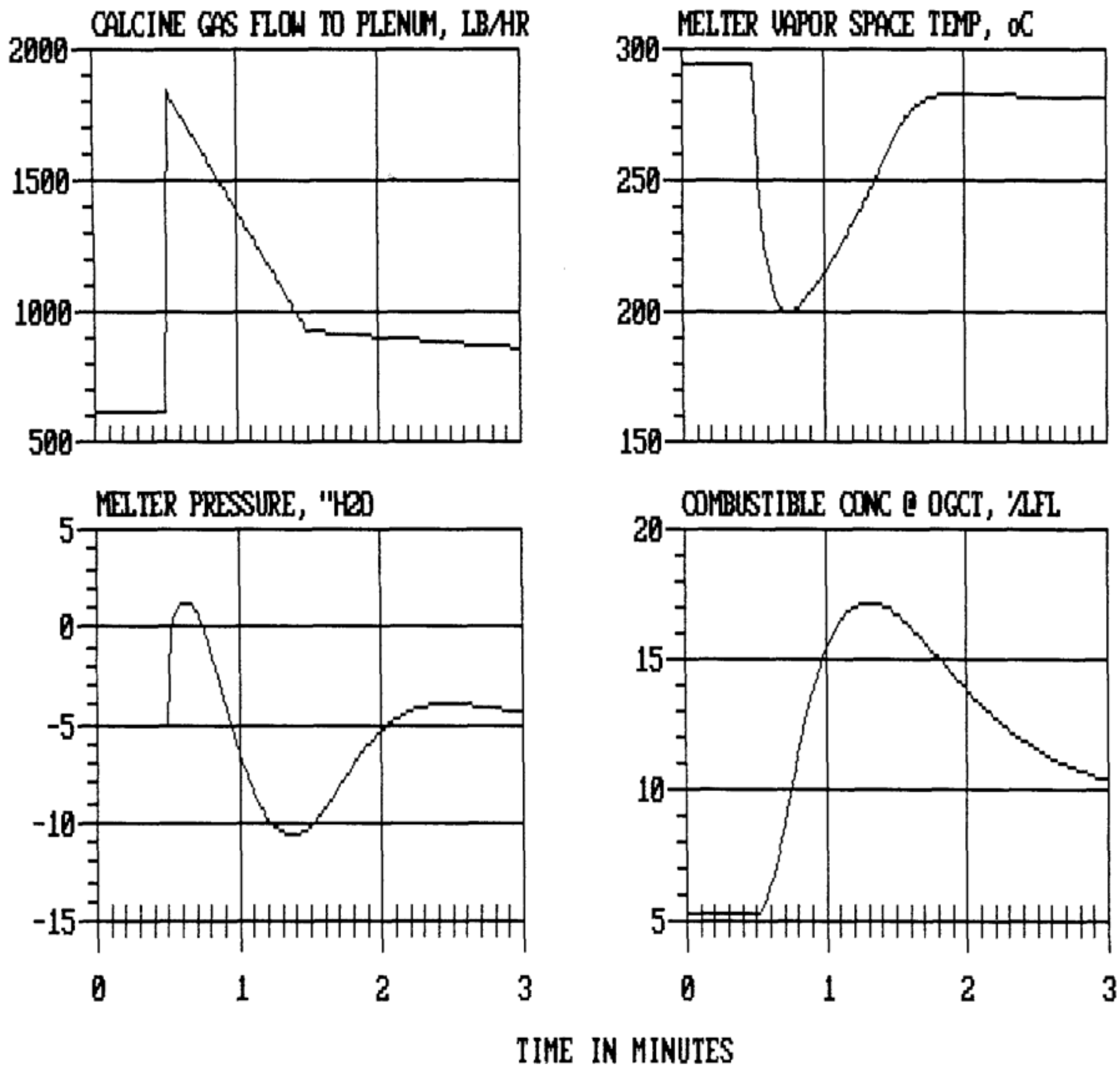
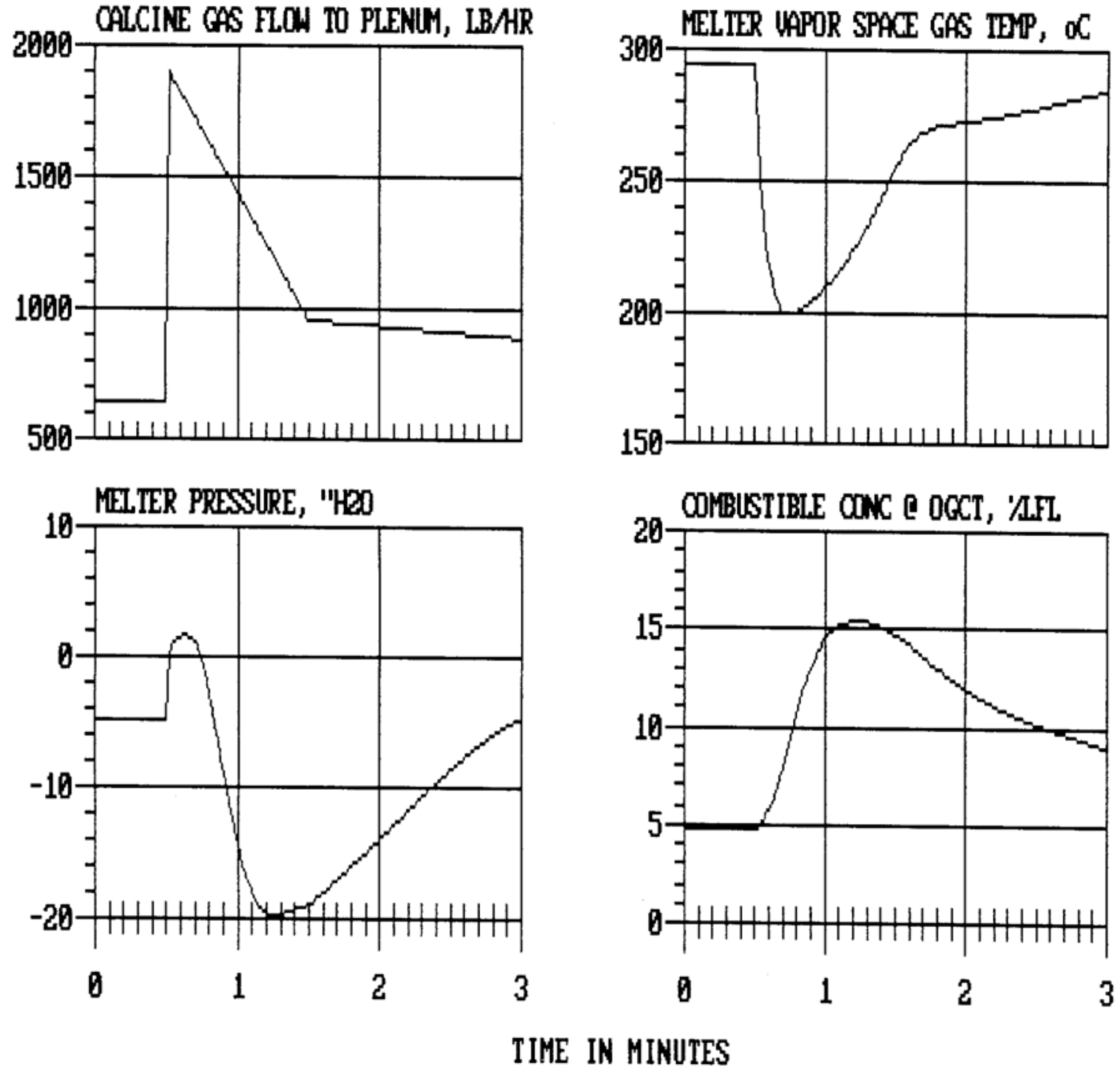


Figure 2. Results of 3X Off-Gas Surge Simulation for Normal Operation with Case 2 Feed (SB10Tk48-4: 150% Acid Stoichiometry, 15,999 ppm TOC, 1.5 GPM Feed Rate; TI4085D = 460 °C; FIC3221A = 900 PPH; FIC3221B = 233 PPH).



TOC than the rate of increase in the total reductant, i.e., the sum of formate and coal, resulting in a more oxidizing feed. This is particularly true for Case 3, where its nitrate level is highest at 52,047 ppm and, as a result, the potential for off-gas flammability is practically non existent. It means that once the minimum formic acid requirement is met to ensure reduction of Hg and Mn, the maximum amount of coal that can be added to the Case 2 feed from the off-gas flammability standpoint can be considerably greater than 7,441 ppm, as long as the target redox is maintained. However, allowing for such a high coal addition would require at least that: (1) an administrative control is put in place so as to ensure that the actual redox is close to the target redox, (2) coal particles remain well dispersed, and (3) its concentration is accurately measured. The new TOC limit for such a case would consist mostly of coal and some minimum quantity of formic acid.

Furthermore, the maximum amount of coal that can be added to the Case 2 feed, while ignoring the redox requirement, was 2,948 ppm before the current TOC limit of 18,900 ppm is exceeded (Case 4). This is considerably less than 7,441 ppm of coal added to the Case 3 feed; in doing so, however, the nitrate level in the Case 4 feed remains the same as that of Case 2. As a result, the flammable gas concentration for Case 4 peaks at 40% of the LFL, which is an order of magnitude higher than that of Case 3 but still well below the 60% of LFL limit. It means that more than 2,948 ppm of coal can be added to the baseline SB10 feed at 150% acid stoichiometry before the flammability safety basis limit of 60% of the LFL is exceeded. Case 5 precisely simulates such a condition, and the model results show that up to 5,063 ppm of coal could be added to the Case 2 feed, while ignoring the redox requirement, before the 60% of the LFL limit is exceeded. In doing so, the maximum TOC limit has been increased from 18,900 to 20,900 ppm.

Also shown in Table 3-25 are the results of Case 6 in which coal was added to the Case 1 feed (SB10Tk48-1), while ignoring the redox requirement, until the calculated flammable gas concentration peaked at near the 60% of the LFL limit during the 3X off-gas surge. It turns out that the maximum amount of coal that can be added to the baseline SB10 feed at 100% acid stoichiometry is ~5,100 ppm, close to the maximum coal value calculated for Case 5. In doing so, however, the maximum TOC limit has been reduced from 18,900 to 17,000 ppm. Sine the redox requirement is ignored, the nitrate level in the Case 6 feed remains practically the same as that of the Case 1 feed.

The calculated calcine gas and glass compositions for Cases 5 and 6 are compared in Tables B-4 and B-5, respectively, in Appendix B. However, the melter feed compositions of these cases are not included, since they are in essence identical to those of Cases 1 and 2, except for coal.

4.0 Conclusions

A paper study was completed to assess the impact on the DWPF's CPC acid addition and melter off-gas flammability control strategy in processing SB10 to SB13 with an added FBSR stream and two SWPF products (Strip Effluent and Actinide Removal Stream). In all of the cases that were modeled, an acid mix using formic acid and nitric acid could be achieved that would produce a predicted Reducing/Oxidizing (REDOX) Ratio of 0.2 $Fe^{+2}/\Sigma Fe$. There was sufficient formic acid in these combinations to reduce both the manganese and mercury present. Reduction of manganese and mercury are both necessary during SRAT processing, however, other reducing agents such as coal and oxalate are not effective in this reduction. The next phase in this study will be experimental testing with SB10, FBSR, and both SWPF simulants to validate the assumptions in this paper study and determine whether there are any issues in processing these streams simultaneously.

The paper study also evaluated a series of abnormal processing conditions to determine whether potential abnormal conditions in FBSR, SWPF or DWPF would produce melter feed that was too oxidizing or too reducing. In most of the cases that were modeled with one parameter at its extreme, an acid mix using formic acid and nitric acid could be achieved that would produce a predicted REDOX of 0.09-0.30 (target 0.20). However, when a run was completed with both high coal and oxalate, with minimum formic acid to reduce mercury and manganese, the final REDOX was predicted to be 0.49 with sludge and FBSR product and 0.47 with sludge, FBSR product and both SWPF products which exceeds the upper REDOX limit. The following cases were considered and the results reported below:

1. **Low Formate Destruction.** Even with no formate destruction in the SRAT or SME, there was enough formic acid added to reduce Mn and Hg and produce a REDOX of 0.20 $Fe^{+2}/\Sigma Fe$.
2. **High FBSR Coal Concentration.** High FBSR coal will produce a melter feed with a predicted REDOX of 0.20. But insufficient formic acid is added to reduce both manganese and mercury unless acid stoichiometry is increased.
3. **High Actinide Removal Product (ARP) oxalate Concentration.** The ARP oxalate contributes <0.01% of the carbon. Even a large increase of oxalate from the SWPF stream will have minimal impact on REDOX.
4. **High Nitrate Destruction.** In the baseline analysis, it was assumed that 2.6% of the nitrite was converted to nitrate. This factor has varied from -30% to 33% in CPC Experiments. A test case was completed assuming maximum catalytic activity to form ammonia and a -30% nitrite to nitrate conversion in the SRAT (all nitrate destroyed, no nitrate generation, 30% of nitrite reduced to ammonia) and 20% nitrate destruction in the Slurry Mix Evaporator (SME). Even under these extreme conditions, the acid mix can be adjusted to produce a predicted REDOX of 0.20. Low initial nitrate concentration in the feeds to the DWPF CPC leads to the same issue as high nitrate destruction.
5. **High SWPF Organic Concentration.** The SWPF organic from solvent extraction is very small compared to the coal in the FBSR. In addition, most of the organic is removed during boiling in the CPC, so very little organic will be present in the melter feed so there should be minimum impact.
6. **High Coal, Oxalate, SWPF Organic Concentration:** In this case, if enough formic acid is added to reduce the manganese and mercury, the resulting REDOX is more reducing than is typically targeted and may lead to more Ni, Cu and noble metal reduction in the melter. A REDOX of 0.20 can not be achieved with any formic acid/nitric acid mixture unless acid stoichiometry is increased.
7. **High Acid Stoichiometry.** DWPF often targets 120-150% higher acid stoichiometry to maximize the nitrite destruction rate and the mercury stripping. A REDOX of 0.20 can be achieved; however the TOC concentration in the melter feed is approximately 18,000 mg/kg, approaching the DWPF limit of 18,500 mg/kg.
8. **High Sludge Oxalate.** A high sludge oxalate concentration is possible if oxalic acid is used in tank cleaning. Current planning is to destroy the oxalate prior to sludge washing. In case the oxalate destruction process is inadequate or delayed, a test case was completed with 10,000 mg/kg oxalate in sludge. A REDOX of 0.20 can be achieved; however the TOC concentration in the melter feed is approximately 17,900 mg/kg, approaching the DWPF limit of 18,500 mg/kg.

A total of six cases were considered in the assessment of DWPF melter off-gas flammability using two computer models that describe the cold cap chemistry and the off-gas combustion and dynamics. The baseline sludge chosen was SB10 at 100% and 150% acid stoichiometry. Coal was then added to these SB10 variations until either the current TOC limit of 18,900 ppm or the flammability safety basis limit of 60% of the LFL was exceeded. The results of model runs show that if: (1) an administrative control is put in place on glass redox, (2) coal particles remain well dispersed, and (3) the concentration of coal can be accurately measured, considerably greater than 7,441 ppm of coal may be added to the DWPF melter feed. On the other hand, if coal is added to the redox-adjusted SB10 at 100-150% acid stoichiometry without giving further consideration to the redox control, the maximum amount of coal that can be added without exceeding the 60% of the LFL safety basis limit is estimated to be ~5,000 ppm.

The assumptions made in performing these calculations need to be validated in the CPC with all feed streams present and with the level of coal currently projected in the FBSR product. After this series of testing is completed, the potential for DWPF melter off-gas flammability should be reassessed to validate the assumptions and also to consider the impact of the melter bubblers.

5.0 Recommendations

The assumptions made in performing these calculations need to be validated in the CPC with all four streams present and with the level of coal currently projected, as well as bounding levels, in the FBSR product. After this series of testing is completed, the melter off-gas flammability calculations should be repeated to validate assumptions and to consider the impact of the melter bubblers.

The worst case sludge batch for this analysis was SB10. The sludge for future testing should be a SB10 simulant. The predicted sludge includes monosodium titanate (MST) which will be added from the actinide removal process in SWPF. To prevent overestimating the MST present, the sludge composition for simulant production will be recalculated by removing the MST and renormalizing the remaining sludge components.

The results of this feasibility analysis indicate that the processing of SB10-13 sludge together with the FBSR product using a coal concentration of 15 wt % and SWPF products is possible in the CPC. A target REDOX of 0.2 is possible and the melter feed TOC limit should be maintained.

In addition, FBSR product produced in Hazen testing will be used along with ARP/ Modular Caustic Solvent Extraction Unit (MCU) simulants used in previous studies. No organic will be added to the MCU simulant and data from previous testing will be used to provide expected concentration in the melter feed.

This study will be followed up by additional studies necessary to develop the Waste Acceptance Criteria for the Tank 48 FBSR product. This will include:

1. Chemical processing cells testing with simulants to demonstrate processing at above calculated coal-carbon limit.

2. Reassessment of Melter Flammability study using the results for the CPC testing for both a bubbled and non-bubbled melter.

It is also recommended that the high coal content in the FBSR product should be re-evaluated. If FBSR product with 15 wt% coal-carbon is combined with sludge and processed in the CPC, the CPC product approaches the TOC limit for CPC processing. Minimizing the coal-carbon concentration will also limit the nonradioactive impurities added in waste processing (coal ash, carbon, sulfur, etc.).

This preliminary study should be reassessed when a new CPC flowsheet is defined and when the FBSR product stream is finalized. Once these studies are complete, this report will be reissued.

6.0 Acknowledgements

The sludge projections for future sludge batches were estimated by Jeff Gillam and David Larsen. The SWPF cesium and actinide stream projections were provided by Azi Samadi and Celia Aponte.

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Appendix A SB11 Acid Calculation Output

Run Description:	**SB11 Sludge Only**	**SB11 Tk48 FBSR No SWPF**	**SB11 Tk48 FBSR SWPF**
Run #	**SB11Tk48-1**	**SB11Tk48-2**	**SB11Tk48-3**
SRAT Vessel Volume, L	**4**	**4**	**4**
Will ARP be added?	**Yes**	**No**	**No**
Will MCU be added?	**Yes**	**No**	**No**
Sludge Analyses for Acid Calculations, Run #	**SB11Tk48-1**	**SB11Tk48-2**	**SB11Tk48-3**
Fresh Sludge Mass, g	3,427.3	3,446.6	3,180.8
Fresh Sludge Weight % Total Solids	24.83	24.28	24.23
Fresh Sludge Weight % Calcined Solids	14.60	14.52	14.51
Fresh Sludge Weight % Insoluble Solids	15.28	15.17	15.16
Fresh Sludge Density, g/mL	1.15	1.14	1.14
Fresh Sludge Supernate density, g/mL	1.04	1.04	1.04
Fresh Sludge Nitrite (mg/kg)	13332.07	12171.17	12074.13
Fresh Sludge Nitrate (mg/kg)	9283.10	8475.51	8408.00
Fresh Sludge Formate (mg/kg)	0.00	0.00	0.00
Fresh Sludge Sulfate (mg/kg)	439.80	496.72	501.47
Fresh Sludge Chloride (mg/kg)	14.24	21.40	22.00
Fresh Sludge Phosphate (mg/kg)	106.79	120.07	121.18
Fresh Sludge Oxalate (mg/kg)	0.00	0.00	0.00
Fresh Sludge Slurry TIC (treated as carbonate, mg/kg)	1315.89	1765.17	1802.72
Fresh Supernate TIC (treated as carbonate, mg/kg)	597.67	1201.44	1251.92
Fresh Sludge Hydroxide (Base Equivalents) pH = 7	0.47	0.46	0.46
Fresh Sludge Coal/Carbon source, wt% total solids basis	0.00	3.63	3.93
Fresh Sludge Manganese (% of Calcined Solids)	2.76	2.52	2.50
Fresh Sludge Magnesium (% of Calcined Solids)	0.33	0.30	0.30
Fresh Sludge Sodium (% of Calcined Solids)	18.71	17.08	16.94
Fresh Sludge Potassium (% of Calcined Solids)	0.15	0.14	0.14
Fresh Sludge Calcium (% of Calcined Solids)	2.07	1.89	1.87
Fresh Sludge Nickel (% of Calcined Solids)	0.40	0.38	0.38
Fresh Sludge Supernate manganese, mg/L	0.00	0.38	0.41
ARP Analyses for Acid Calculations, Run #	SB11Tk48-1	SB11Tk48-2	SB11Tk48-3
ARP Mass without trim chemicals, g			483.9
ARP Weight % Total Solids			10.09
ARP Weight % Calcined Solids			7.28
ARP Weight % Insoluble Solids			6.04
ARP Density, g/mL			1.06
ARP Supernate density, g/mL			1.02
ARP Nitrite (mg/kg)			3,181.1
ARP Nitrate (mg/kg)			3,758.9
ARP Oxalate (mg/kg)			55.4
ARP Formate (mg/kg)			31.85
ARP Sulfate (mg/kg)			10.75
ARP Chloride (mg/kg)			26.99
ARP Phosphate (mg/kg)			6669.86
ARP Slurry TIC (treated as carbonate, mg/kg)			2557.87

Run Description:	**SB11 Sludge Only**	**SB11 Tk48 FBSR No SWPF**	**SB11 Tk48 FBSR SWPF**
ARP Supernate TIC (treated as carbonate, mg/kg)			2785.90
ARP Hydroxide (Base Equivalents) pH = 7			0.33
ARP Mercury (% of Total Solids in untrimmed sludge)			0.00
ARP Manganese (% of Calcined Solids)			3.55
ARP Magnesium (% of Calcined Solids)			0.34
ARP Sodium (% of Calcined Solids)			14.54
ARP Potassium (% of Calcined Solids)			0.20
ARP Cesium (% of Calcined Solids)			0.00
ARP Calcium (% of Calcined Solids)			2.14
ARP Strontium (% of Calcined Solids)			0.00
ARP Nickel (% of Calcined Solids)			0.39
ARP Supernate manganese, mg/L			0.00
MCU Analyses for Acid Calculations, Run #	**SB11Tk48-1**	**SB11Tk48-2**	**SB11Tk48-3**
MCU Mass, g			2137.28
MCU Weight % Total Solids			0.21
MCU Weight % Calcined Solids			0.2
MCU Weight % Insoluble Solids			0.0
MCU Density, g/mL			1.001
MCU Supernate density, g/mL			1.001
MCU Nitrite (mg/kg)			0
MCU Nitrate (mg/kg)			682
MCU Sulfate (mg/kg)			2
MCU Chloride (mg/kg)			0.00
MCU Cesium (% of Calcined Solids)			100
SRAT Processing Assumptions, Run #	**SB11Tk48-1**	**SB11Tk48-2**	**SB11Tk48-3**
Conversion of Nitrite to Nitrate in SRAT Cycle, %	2.60	2.60	2.60
Destruction of Nitrite in SRAT and SME cycle, %	100.00	100.00	100.00
Destruction of Formic acid charged in SRAT, %	22.10	22.10	22.10
Destruction of Oxalate charged, %	50.00	50.00	50.00
Percent Acid in Excess Stoichiometric Ratio	100.00	100.00	100.00
SRAT Product Target Solids, Weight % Total Solids	30.00	30.00	30.00
Nitric Acid Molarity	10.400	10.400	10.400
Formic Acid Molarity	23.550	23.550	23.550
DWPF Nitric Acid addition Rate, gallons/min	2.0	2.0	2.0
DWPF Formic Acid addition Rate, gallons/min	2.0	2.0	2.0
REDOX Target	0.200	0.200	0.200
Trimmed Sludge Target wt% Ag dry basis	0.0142	0.0142	0.0142
Trimmed Sludge Target wt% Hg dry basis	3.9000	3.9000	3.9000
Trimmed Sludge Target wt% Pd dry basis	0.0066	0.0066	0.0066
Trimmed Sludge Target wt% Rh dry basis	0.0233	0.0233	0.0233
Trimmed Sludge Target wt% Ru dry basis	0.1121	0.1121	0.1121
Trimmed Sludge Target Wt% Coal/carbon dry basis	0.0000	3.4575	3.5231
SRAT air purge, scfm	230	230	230
SRAT boil-up rate, lb/hr	5000	5000	5000
SRAT total boil-up (reflux), lb	60,000	60,000	60,000

Run Description:	**SB11 Sludge Only**	**SB11 Tk48 FBSR No SWPF**	**SB11 Tk48 FBSR SWPF**
SRAT Steam Stripping Factor (lb steam/lb Hg)	750	750	750
SME Processing Assumptions, Run #	**SB11Tk48-1**	**SB11Tk48-2**	**SB11Tk48-3**
Frit type	418	418	418
% Destruction of Formic acid in SME	8.40	8.40	8.40
% Destruction of Nitrate in SME	11.90	11.90	11.90
Assumed SME density, g/mL	1.420	1.420	1.420
Sludge Oxide Contribution in SME (Waste Loading)	40.00	40.00	40.00
Frit Slurry Formic Acid Ratio	1.50	1.50	1.50
Target SME Solids total Wt%	50.0	50.0	50.0
Volume of water per deconed can	1,000	1,000	1,000
SME air purge	74	74	74
SME boil-up rate	5000	5000	5000
Acid and Glass Calculation Base Values			
Total nitrite	0.993	0.912	0.868
Total Mn minus soluble Mn	0.251	0.230	0.256
Total carbonate	0.375	0.507	0.580
Total hydroxide	1.395	1.391	1.422
Total mercury	0.165	0.163	0.150
Total oxalate	0.000	0.000	0.000
Total grams of calcined oxides	500.500	500.500	496.890
Trim Chemicals Calculations	40.8658	41.6932	40.8662
Fresh Sludge Calcine Factor (1100°C), g oxide/g dry solids (calculated)	0.5881	0.5981	0.5989
ARP calcine factor	0.0000	0.0000	0.7211
Total solids before trim addition	851.1021	836.8703	819.6844
Total solids before trim less HgO, NaOxalate, coal)	851.10	807.94	790.81
Predicted total solids at target levels	891.9679	878.5636	860.5506
Predicted total mass at target levels	3,471.85	3,491.88	3,708.7
Target Ag metal content in trimmed sludge	0.014190	0.014190	0.014190
$AgNO_3$ to add (CF=0.682)	0.19933	0.19633	0.19230
Ag_2O calcined solids	0.13596	0.13391	0.13117
Water added with Ag	0.00000	0.00000	0.00000
Target wt% Hg dry basis	3.900	3.900	3.900
Total HgO in trimmed Sludge	37.56	37.00	36.24
HgO to add	37.56	37.00	36.24
HgO calcined solids	0.00000	0.00000	0.00000
Calculated total wt% Hg dry basis	3.9000	3.9000	3.9000
Target Pd metal content in trimmed sludge	0.0066	0.0066	0.0066
Wt % Pd in reagent solution	15.2700	15.2700	15.2700
$Pd(NO_3)_2*H_2O$ solution to add (CF=1.150 g metal oxide/g metal), g	0.38681	0.38100	0.37319
Pd(NO3)2 to add, g	0.12790	0.12597	0.12339
PdO calcined solids, g	0.06795	0.06693	0.06555
Water added with Pd, g	0.259	0.255	0.250
Target Rh metal content in trimmed sludge, g	0.0233	0.0233	0.0233

Run Description:	**SB11 Sludge Only**	**SB11 Tk48 FBSR No SWPF**	**SB11 Tk48 FBSR SWPF**
Wt% Rh in reagent solution	4.93	4.93	4.93
$Rh(NO_3)_3$*$2H_2O$ (CF=1.311g metal oxide/g metal), g	4.0145	3.8109	3.7301
Rh(NO3)3 to add, g	0.55567	0.52749	0.51631
Rh2O3 calcined solids, g	0.24407	0.23169	0.22678
Water added with Rh, g	3.459	3.283	3.214
Target Ru metal content in trimmed sludge, g	0.1121	0.1121	0.1121
Wt% Ru in $RuCl_3$ reagent solids	41.74	41.74	41.74
$RuCl_3$ to add (CF=1.0), g	2.3949	2.3589	2.3105
Target wt% Coal/carbon source in trimmed sludge, dry basis, g	0.00	3.46	3.52
Total Coal in fresh Sludge, g	0.000	30.376	30.318
Total Coal in trimmed Sludge, g	0.000	30.376	30.318
Calculated wt% coal after trim additions	0.00	3.46	3.52
Oxides added with coal (Assumed no calcine factor, ash in analysis)	0.00	0.00	0.00
Total Sodium Oxalate in fresh Sludge	0.000	0.000	0.000
Total Sodium Oxalate in trimmed Sludge	0.000	0.000	0.000
Calculated oxalate conc. after trim chemical additions	0.00	0.00	0.00
Na_2O calcined solids from sodium oxalate	0.00000	0.00000	0.00000
Total mass of trim chemicals added	44.6	43.7	42.8
Calcined oxides added in trim chemicals	2.84	2.79	2.73
Total solids after trim addition	891.94	877.08	859.07
Match of actual to predicted total solids mass	100.00%	100.17%	100.17%
Total Calcined solids after trim	503.34	503.29	499.62
Mass of trimmed sludge	3,471.82	3,490.39	3,707.48
Calculated wt% total solids in trimmed sludge	25.7	25.1	23.2
Mass of trimmed feeds reacted	3,471.82	3,490.39	3,707.48
Mass of equivalent sludge w/o ARP	3,591.72	3,612.23	3,544.80
Calcined solids at start of SRAT	503.3	503.3	499.6
STOICHIOMETRIC ACID CALCULATIONS			
Koopman Stoichiometric Acid Ratios Used (Nominal)			
Acid requirement per mole of Nitrite	1.10	1.10	1.10
Acid requirement per mole of Mn	3.00	3.00	3.00
Acid requirement per mole of Carbonate	1.00	1.00	1.00
Acid requirement per mole of Hydroxide	1.00	1.00	1.00
Acid requirement per mole of Hg	1.00	1.00	1.00
Acid requirement per mole of Oxalate	0.00	0.00	0.00
Acid requirement per mole of Calcium	1.75	1.75	1.75
Acid requirement per mole of Mg	1.75	1.75	1.75
Fresh feed NO_2^-, g-mole	0.99	0.91	0.87
Fresh feed Manganese, g-mole	0.25144	0.22967	0.23294
Fresh feed slurry Carbonate, g-mole	0.3755	0.5065	0.5805
Fresh feed OH^-, g-mole	1.3947	1.3905	1.4216

Run Description:	**SB11 Sludge Only**	**SB11 Tk48 FBSR No SWPF**	**SB11 Tk48 FBSR SWPF**
Fresh feed H+, g-mole	0.0000	0.0000	0.0000
Total Sludge Mercury, g-mole	0.173422	0.170816	0.167314
Acid requirement per mole of Oxalate	0.00	0.00	0.00
Fresh Feed Supernate Carbonate, g-mole	0.14	0.28	0.37
Fresh Feed Calcium, g-mole	0.26	0.24	0.23
Fresh Feed Magnesium, g-mole	0.07	0.06	0.06
Fresh Feed Nitrate, g-mole	0.00	0.00	0.00
Fresh Feed Formate, g-mole	0.00	0.00	0.04
Hsu Total Stoichiometric Acid required	3.3657	3.5339	3.6806
Koopman Nominal Stoichiometric Acid required	4.1250	4.0565	4.1356
Koopman Minimum Stoichiometric Acid required	3.5669	3.5462	3.6251
Percent Acid in Excess Stoichiometric Ratio	100.000	100.000	100.000
Actual acid to add to SRAT, g-mole	3.5669	3.5462	3.6251
Acid required in moles per liter of starting sludge (untrimmed, less receipt samples)	1.1944	1.1729	1.2985
REDOX Target	0.200	0.200	0.200
Predicted REDOX	0.200	0.200	0.200
Ratio of formic acid to total acid	0.8798	0.3761	0.3944
Formic acid density, g/mL at 20 °C	1.2044	1.2044	1.2044
Nitric acid, wt %	50.03	50.03	50.03
Formic acid, wt %	89.99	89.99	89.99
Formic acid amount, g-mole	3.138	1.334	1.430
Nitric acid amount, g-mole	0.429	2.212	2.195
Projected Melter Feed Manganese, total moles	0.251	0.230	0.256
Formate moles added with formic acid	3.138	1.334	1.430
Formate moles destroyed in SRAT (% of acid charged)	0.694	0.295	0.316
Formate moles reacted in SME (% of acid charged)	0.224	0.106	0.112
Formate Moles after SME	2.221	0.933	1.002
Frit slurry formate (when SME cycle frit additions are made with formic acid)	0.221	0.221	0.220
Projected Melter Feed Formate, total moles	2.442	1.155	1.221
Nitrate moles from nitric acid	0.429	2.212	2.195
Nitrate from conversion of nitrite to nitrate in SRAT and SME	0.026	0.024	0.023
Nitrate from minor trim chemicals	0.00805	0.00773	0.00756
Nitrate destroyed in the SME	0.11613	0.32308	0.32246
Projected Melter Feed Nitrate, total moles (Sum of inputs - destroyed)	0.860	2.392	2.387
Oxalate from trim	0.000	0.000	0.000
Oxalate destroyed during reaction	0.000	0.000	0.000
Projected Melter Feed Oxalate, total moles	0.000	0.000	0.000
Carbon from trim coal	0.000	0.000	0.000
Projected Melter Feed Carbon from coal, total moles	0.000	2.529	2.524
Projected final SME mass, kg	**3.376**	**3.431**	**3.387**
Manganese concentration in final melter feed, wt %	0.074	0.067	0.075

Run Description:	**SB11 Sludge Only**	**SB11 Tk48 FBSR No SWPF**	**SB11 Tk48 FBSR SWPF**
Formate concentration in final melter feed	0.723	0.337	0.361
Oxalate concentration in final melter feed	0.000	0.000	0.000
Carbon from coal concentration in final melter feed	0.000	0.737	0.745
Nitrate concentration in final melter feed	0.255	0.697	0.705
Nitrite concentration in final melter feed	0.000	0.000	0.000
Projected final SME volume, L	**2.501**	**2.541**	**2.509**
BENCH SCALE CALCULATIONS			
Scaled formic acid feed rate, mL/min	1.0039	1.0162	1.0905
Scaled nitric acid feed rate, mL/min	1.0034	1.0156	1.0899
Prototypical formic acid feed time, min	132.7	55.7	55.7
Prototypical nitric acid feed time, min	41.1	209.5	193.7
Formic acid volume required, mL	133.250	56.636	60.704
Nitric acid volume required, mL	41.237	212.730	211.104
Dewatering Calc for Target Wt. % Total Solids in SRAT Product			
Final SRAT Product Weight % Total Solids	30.00	30.00	30.00
Water in Trimmed (and sampled) Sludge, g	2,579.88	2,613.31	2,848.42
Water added with antifoam, g	54.59	54.91	53.88
Water added with formic acid, g	16.06	6.82	7.32
Water added with nitric acid, g	26.99	139.24	138.18
Water added in acid flushing, g	0.00	0.00	0.00
Water made during base equiv neutralization, g	25.13	25.05	25.61
Water made in TIC destruction, g	6.76	9.13	10.46
Water made in SRAT nitrite destruction, g	5.96	5.48	5.21
Water made in Mercury Reduction, g	3.12	3.08	3.01
Revised water mass in slurry, g	2,718.50	2,857.02	3,092.09
Solids in Trimmed (and sampled) Sludge, g	891.94	877.08	859.07
Mass 1:20 antifoam added, g	2.87	2.89	2.84
Mass of pure formic acid (HCOOH) added, g	144.43	61.39	65.80
Mass of pure nitric acid (HNO3) added, g	27.02	139.41	138.34
Solids lost during base equiv neutralization, g	25.13	25.05	22.92
Solids lost in TIC destruction, g	23.29	31.42	36.00
Solids lost in SRAT nitrite destruction, g	25.83	23.72	22.58
Solids lost in SRAT nitrite destruction, g	44.14	40.53	38.59
Solids lost in SRAT formate destruction, g	31.92	13.57	14.54
Solids lost in Mercury Stripping, g	37.56	37.00	36.24
Revised solids mass in slurry, g	922.54	950.01	933.76
Target water mass in slurry to hit total solids target, g	2,152.59	2,216.70	2,178.77
Calculated total water to remove to return to starting volume, g	266.94	363.92	364.28
Mass of carbonate lost as CO_2, g	16.53	22.29	25.55
Mass of nitrite lost as NO, g	19.35	17.77	16.27
Formate converted to CO_2, g	31.92	13.57	14.54

Run Description:	**SB11 Sludge Only**	**SB11 Tk48 FBSR No SWPF**	**SB11 Tk48 FBSR SWPF**
Formate converted to CO2 in SRAT, g	31.92	13.57	14.54
Mass of treated sludge going into SME cycle, g	3075.13	3166.71	3112.52
Calcined Solids going to SME, g	503.34	503.29	499.62
DWPF SCALE TO BENCH SCALE			
DWPF Scale SRAT cycle			
Volume based scale factor 6000 gal starting SRAT	7540.9	7449.8	6942.3
Minimum SRAT conflux time, min	4583.8	4432.9	4044.2
mercury stripping time at assumed stripping factor, min	76.40	73.88	67.40
Bench Scale SRAT cycle			
99.5% of scaled air purge, scc/min	859.4	869.9	933.5
Helium purge rate at 0.5 vol%, scc/min	4.3	4.4	4.7
Scaled boil-up rate, g/min	5.01	5.07	5.44
Required dewatering time (ARP and after acid), min	112.9	126.2	167.7
99.5% scaled SME air purge, scc/min	276.5	279.9	300.3
Helium purge rate at 0.5 vol%, scc/min	1.38	1.40	1.50
SRAT product Calcine Factor (calculated)	0.546	0.530	0.535
Sludge calcined solids - based on SRAT product	503.34	503.29	499.62
Sludge oxide contribution in SME	40.00	40.00	40.00
Frit oxide contribution, %	60.00	60.00	60.00
Frit slurry wt % solids	50.00	50.00	50.00
Frit slurry formic acid ratio	1.50	1.50	1.50
Water in frit slurry, g	743.7	743.6	738.2
Total frit slurry water, g	743.7	743.6	738.2
Total mass of frit slurry, g	1510.0	1509.9	1498.9
Approximate time to remove water:	75.3	74.4	68.8
Target SME solids total wt%	50.0	50.0	50.0
Mass of water to boil off for final SME concentration, g	460.2	497.1	480.9
Scaled boil-up rate, g/min	5.01	5.07	5.44

Appendix B: SB10 Melter Feed, Calcine Gases and Glass Compositions

Table B-1. Composition of SB10Tk48-1 Baseline Melter Feed at 1.5 GPM.

Insoluble Solids	lb/hr		Soluble Solids	lb/hr
FeOOH	75.3528		Ca(COOH)2	6.4588
Al(OH)3	32.9536		Ca(NO3)2	
MnO2	1.3055		Co(COOH)2	
Ca(OH)2	3.5751		Co(NO3)2	
Na2U2O7	2.5252		CsCOOH	
Mg(OH)2	1.0762		CsNO3	
HgO	6.0159		Cu(COOH)2	0.0525
Ca3(PO4)2			Cu(NO3)2	
Ni(OH)2	1.7368		KCOOH	
Cr(OH)3	0.6811		KNO3	0.7017
Cu(OH)2	0.1333		Mg(COOH)2	0.5274
TiO2	4.1344		Mg(NO3)2	
SiO2	214.2232		Mn(COOH)2	19.5874
Na2O	38.8732		Mn(NO3)2	
Zn(OH)2	0.1320		NH4NO3	
PuO2			NaCl	0.0267
K2O			NaF	
RuO2			NaCOOH	45.5709
RhO2			NaNO3	26.9284
PdO			NaNO2	
Ce(OH)3	1.8016		Na3PO4	0.1126
SrCO3			Ni(COOH)2	0.6965
B2O3	21.8281		Ni(NO3)2	
Li2O	21.8265		Pb(NO3)2	
BaSO4	0.6764		Sr(COOH)2	
PbSO4	1.0327		UO2(COOH)2	0.7170
TcO2			UO2(NO3)2	
La(OH)3	0.4749		La(COOH)3	0.1713
ZrO2	1.1242		La(NO3)3	
CaCO3			Zn(COOH)2	0.0516
CaSO4	0.1910		Zn(NO3)2	
AlOOH			Na2SO4	0.5851
Total_1	431.6736		Total_2	102.1880
			H2O	533.8616
			Total	1067.7231

Table B-2. Composition of SB10Tk48-4 Melter Feed at 1.5 GPM.

Insoluble Solids	lb/hr		Soluble Solids	lb/hr
FeOOH	75.3528		Ca(COOH)2	6.4588
Al(OH)3	32.9536		Ca(NO3)2	
MnO2	1.3055		Co(COOH)2	
Ca(OH)2	3.5757		Co(NO3)2	
Na2U2O7	2.5252		CsCOOH	
Mg(OH)2	1.0762		CsNO3	
HgO	6.3555		Cu(COOH)2	0.0525
Ca3(PO4)2			Cu(NO3)2	
Ni(OH)2	1.7368		KCOOH	
Cr(OH)3	0.6811		KNO3	0.7017
Cu(OH)2	0.1333		Mg(COOH)2	0.5274
TiO2	4.1344		Mg(NO3)2	
SiO2	214.2232		Mn(COOH)2	19.5874
Na2O	20.2326		Mn(NO3)2	
ThO2			NH4COOH	
Zn(OH)2	0.1320		NH4NO3	
PuO2			NaCl	0.0267
K2O			NaF	
RuO2			NaCOOH	74.6586
RhO2			NaNO3	41.6967
PdO			NaNO2	
Ce(OH)3	1.8016		Na3PO4	0.1126
SrCO3			Ni(COOH)2	0.6965
B2O3	21.8281		Ni(NO3)2	
Li2O	21.8265		Pb(NO3)2	
BaSO4	0.6764		Sr(COOH)2	
PbSO4	1.0327		UO2(COOH)2	0.7170
La(OH)3	0.4749		La(COOH)3	0.1713
ZrO2	1.1242		La(NO3)3	
CaCO3			Zn(COOH)2	0.0516
CaSO4	0.1900		Zn(NO3)2	
AlOOH			Na2SO4	0.5851
Total_1	413.3721		Total_2	146.0440
			H2O	559.4161
			Total	1118.8321

Table B-3. Composition of SB10Tk48-6 Melter Feed at 1.5 GPM.

Insoluble Solids	lb/hr		Soluble Solids	lb/hr
FeOOH	76.5343		Ca(COOH)2	6.5999
Al(OH)3	34.9345		Ca(NO3)2	
MnO2	1.2985		Co(COOH)2	
Ca(OH)2	3.1708		Co(NO3)2	
Na2U2O7	2.6188		CsCOOH	
Mg(OH)2	1.0922		CsNO3	
HgO	6.4042		Cu(COOH)2	0.0553
Ca3(PO4)2			Cu(NO3)2	
Ni(OH)2	1.7072		KCOOH	
Cr(OH)3	0.7120		KNO3	0.6500
Cu(OH)2	0.1404		Mg(COOH)2	0.5352
TiO2	4.2507		Mg(NO3)2	
SiO2	214.8207		Mn(COOH)2	19.4824
Na2O	14.9115		Mn(NO3)2	
ThO2			NH4COOH	
Zn(OH)2	0.1532		NH4NO3	
PuO2			NaCl	0.0279
K2O			NaF	
RuO2			NaCOOH	46.2156
RhO2			NaNO3	82.1161
PdO			NaNO2	
Ce(OH)3	1.7892		Na3PO4	0.1125
SrCO3			Ni(COOH)2	0.6847
B2O3	21.8281		Ni(NO3)2	
Li2O	21.8265		Pb(NO3)2	
BaSO4	0.6875		Sr(COOH)2	
PbSO4	1.0256		UO2(COOH)2	0.7436
La(OH)3	0.4763		La(COOH)3	0.1718
ZrO2	1.1497		La(NO3)3	
CaCO3			Zn(COOH)2	0.0599
CaSO4	1.0815		Zn(NO3)2	
AlOOH			Na2SO4	0.5503
Total_1	421.2352		Total_2	158.0056
			H2O	579.2408
			Total	1158.4816

Table B-4. Comparison of Calcine Gas Compositions of Cases 5 and 6.

Case	5	6
Calcine Gases	SB10Tk48-4C (gmole/hr)	SB10Tk48-1C (gmole/hr)
H2O	594.967	551.845
CO2	681.821	551.791
H2	227.953	220.492
N2	106.595	73.258
CO	162.252	136.962
O2	0.000	0.000
SO2	0.003	0.001
NO	0.000	0.000
NO2	0.000	0.000
NaBO2 g	0.000	0.000
total	1,773.591	1,534.350
Calculated TOC (ppm)	20,900	17,000
CO/CO2	0.238	0.248
H2/(CO+CO2)	0.270	0.320
Required Combustion Air (lb/hr)	222	203

Table B-5. Comparison of Glass Compositions of Cases 5 and 6.

Phases	SB10Tk48-4C (gmole/hr)	SB10Tk48-1C (gmole/hr)
Melt		
SiO2 l	972.704	994.072
Na2SiO3	484.061	511.281
LiBO2 l	268.330	283.413
LiAlO2 l	181.012	191.190
Fe3O4 l	65.429	39.522
MgSiO3 l	7.992	8.222
FeO l	79.491	112.035
CaFe2O4	2.469	1.178
B2O3 l	0.000	0.000
Ca2SiO4	16.302	18.559
Ca3MgSi2	1.893	2.219
Fe2SiO4	41.351	112.035
KBO2	0.324	93.222
Li2O l	88.257	1.396
K2SiO3	1.325	0.347
Spinel		
NiFe2O4	0.000	0.000
Mn3O4	0.000	0.000
CuFe2O4	0.000	0.000
MgFe2O4	0.000	0.000
ICP		
Fe2O3	0.000	0.000
NiO	9.196	6.848
CaSO4	1.806	0.000
Ni3S2	0.280	0.774
MnO	64.347	67.945
Redox		
Fe(+2)/Fe(total)	0.63	0.82

Distribution:

A. B. Barnes, 999-W
D. A. Crowley, 773-43A
S. D. Fink, 773-A
B. J. Giddings, 786-5A
C. C. Herman, 999-W
S. L. Marra, 773-A
A. M. Murray, 773-A
F. M. Pennebaker, 773-42A
W. R. Wilmarth, 773-A
C. J. Bannochie, 773-42A
J. M. Gillam, 766-H
B. A. Hamm, 766-H
J. F. Iaukea, 704-30S
D. D. Larsen, 766-H
R. T. McNew, 704-27S
J. E. Occhipinti, 704-S
D. K. Peeler, 999-W
J. W. Ray, 704-S
H. B. Shah, 766-H
D. C. Sherburne, 704-S
M. E. Stone, 999-W
J. M. Bricker, 704-27S
T. L. Fellinger, 704-26S
E. W. Holtzscheiter, 704-15S
M. T. Keefer, 766-H
C. L. Atseff, 766-H
E. A. Brass, 766-H
S. C Shah, 766-H
A. Samadi-Dezfouli, 766-H
C. I. Aponte, 766-H
E. W. Daniel, 999-W
J. D. Newell, 999-W
A I. Fernandez, 999-W
D. C. Koopman, 999-W
J. M. Pareizs, 773-A
C. J. Bannochie, 773-42A
D. P. Lambert, 999-W
A. S. Choi, 773-42A