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Salt Composition Derived from Veazey Composition by Thermodynamic Modeling and Predicted Composition of Drum Contents

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1.0 SUMMARY

This report describes the derivation of the salt composition from the Veazey salt stream analysis. It also provides an estimate of the proportions of the kitty litter, nitrate salt and neutralizer that was contained in drum 68660.

While the actinide content of waste streams was judiciously followed in the 1980s in TA-55, no record of the salt composition could be found. Consequently, a salt waste stream produced from 1992 to 1994 and reported by Gerry Veazey provided the basis for this study. While chemical analysis of the waste stream was highly variable, an average analysis provided input to the Stream Analyzer software to calculate a composition for a concentrated solid nitrate salt and liquid waste stream. The calculation predicted the gas / condensed phase compositions as well as solid salt / saturated liquid compositions. The derived composition provides an estimate of the nitrate feedstream to WIPP for which kinetic measurements can be made.

The ratio of salt to Swheat in drum 68660 contents was estimated through an overall mass balance on the parent and sibling drums. The RTR video provided independent confirmation concerning the volume of the mixture. The solid salt layer contains the majority of the salt at a ratio with Swheat that potentially could become exothermic.

2.0 INTRODUCTION

In order to elucidate conditions leading to the WIPP event, a salt composition is required for characterization of reaction kinetics for thermal modeling and for assembly of surrogate drum tests. While the radiological makeup of waste salts from TA-55 was well characterized, the chemical make-up was rarely measured. The best compositional data came from the 1992 to 1994 timeframe and was documented in a report by Veazey et. al. [1,2]. During that time, the Vault Work-off Project was processing high-chloride hydroxide cakes that altered the average composition compared to 1985 when the waste, finally deposited in drum 68660, was made. The magnesium and calcium to sodium ratio may have been higher in '92 to '94 with more iron, nickel and chromium from system corrosion. For this reason, an effort was made to estimate a salt composition based upon historical data for the parent salt drum [3]. Results for this study are documented elsewhere.

When the Veazey analysis was performed, nitrate wastes were solubilized and neutralized in the Cement Fixation System. Portland cement was added to solidify the liquid waste in 55 gallon drums. In the 1985 process, the evaporator was operated to concentrate the salts and maximize the amount of solid salt that was produced. Remaining liquid was cemented in 1 gallon cans. Efforts were made to minimize the liquid waste stream. Without salt composition measurements from the 1980s, an estimate of composition from the Veazey analysis was needed. Thermodynamic modeling software called Stream Analyzer®, created by OLI Systems, was identified as capable of modeling the high ionic strength salt mixtures that arose in the 1980's process. Evaporation of water and nitric acid, based upon vapor – liquid equilibrium, gave the final acid and water content of the waste stream. The distribution of solid salt to residual liquid was determined through solid – liquid phase equilibrium calculations. Final adjustments, such as the addition of lead from dissolution of the parent drum lead liner over 30 years of storage were also included in calculating the composition of salts and retained liquid.

3.0 MODELING TOOL

Stream Analyzer software represents many years of development work by OLI Systems to create a tool for predicting the behavior of multicomponent aqueous systems. The company worked with national laboratories to create a data base that addressed the behavior of Hanford wastes. Miraslaw et. al. [4] describe modeling deliquescent multicomponent salt mixtures containing Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Cl^- and NO_3^- ions. They note that the well-known Pitzer ion-interaction model is useful for predicting salt phases and solubility for concentrations up to 6 moles per kg. To predict the behavior for higher concentrations, the OLI thermodynamic framework combines an excess Gibbs energy model with a comprehensive treatment of chemical equilibria that includes long-range electrostatic, ion-ion and ion-molecule, and short-range interactions at temperatures up to 300°C. Their paper illustrates how well the model represents complex experimental data.

A prediction of vapor-liquid equilibrium is also needed from the model. To validate the model, nitric acid / water vapor pressure data was compared to model predictions. Figure 1 illustrates good agreement over the temperature range of interest. All calculations were performed with Stream Analyzer using the MSE databank that implements the Helgeson Direct method.

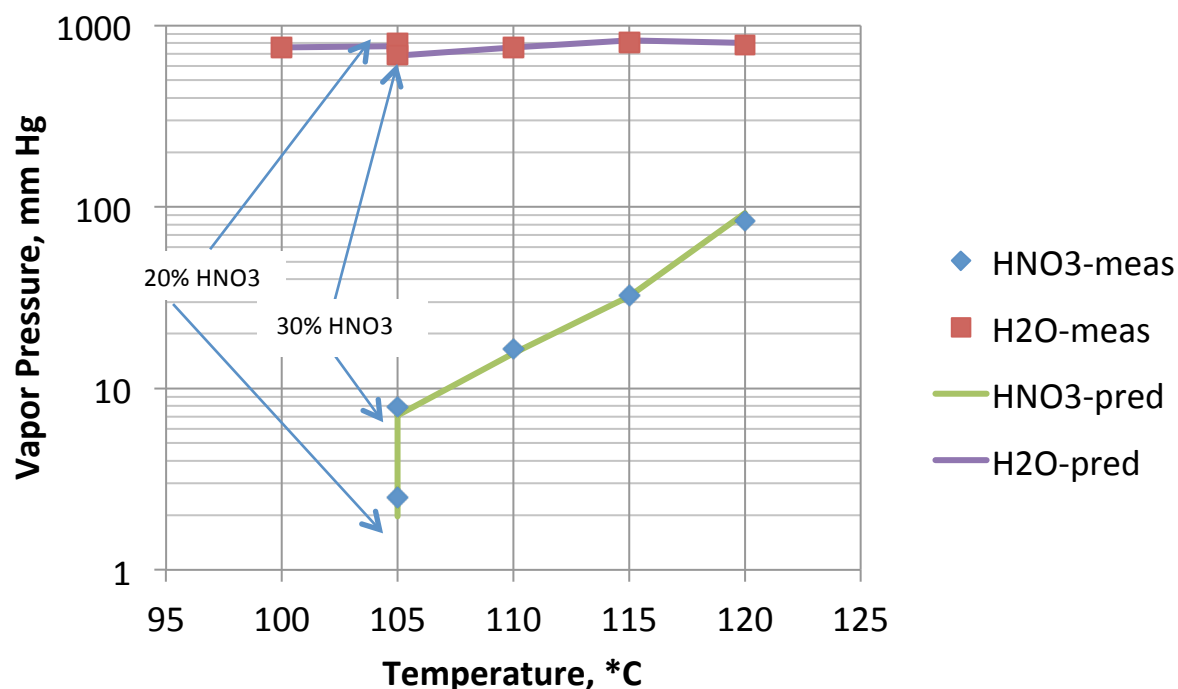


Figure 1. Comparison of nitric acid water vapor from experiments with Stream Analyzer predictions.

4.0 MODELING PROCEDURE AND RESULTS

In order to track the changes in composition, each step was modeled sequentially with assumptions that are noted.

4.1 Parent Drum Feed Modeling

The parent drum, the source for drum 68660 nitrate salts, was S855793. It was packed 11/12/1985 with a mixture of salts derived from 14 batches or bags listed in Table 1. Owing to differences in processing, these batches are divided into totals for Lean Residual (LR) and Oxalate Filtrate (OF). Nearly all the bags had a listing of both weight of salt crystals and liquid volume that drained from the solid phase. It is assumed that some liquid phase was retained by the solid salts by capillary action.

In the Veazey report, average compositions of LR and OF streams were reported. These compositions were assumed to agree with the feed that created the LR and OF evaporator bottom products in Table 1. The calculation procedure is summarized in Figure 2.

Table 1. Item IDs, salt weight and liquid volume pertaining to salts loaded in drum S855793.

Item ID	net (kg)	Liquid	Lean Residual (LR)		Oxalate Filtrate (OF)	
		(L)	kg salt	liquid, L	kg salt	liquid, L
10LALR1W	5.94	9.4	5.94	9.4		
10LR5W1	4.8	20.1	4.8	20.1		
10LR5E1	9.71	15.4	9.71	15.4		
10LR16W1	8.6	Missing	8.6	0		
10LR16E1	7.4	12	7.4	12		
10LR17W1	7	16.5	7	16.5		
10LR17E1	7.2	10.5	7.2	10.5		
10RR18E1	9.68	17	9.68	17		
10OX11W1-1	9.96	3.9			9.96	3.9
10OX11W1-2	10.97				10.97	0
10LR18E1	7.5	11.6	7.5	11.6		
10LR18W1	12.93	13.1	12.93	13.1		
10OX21E1	9.6	11.8			9.6	11.8
10OX21W1	15.1	11.6			15.1	11.6
Total	126.39		80.76	125.6	45.63	27.3
Kg Salt / L liquid				0.642994		1.671429

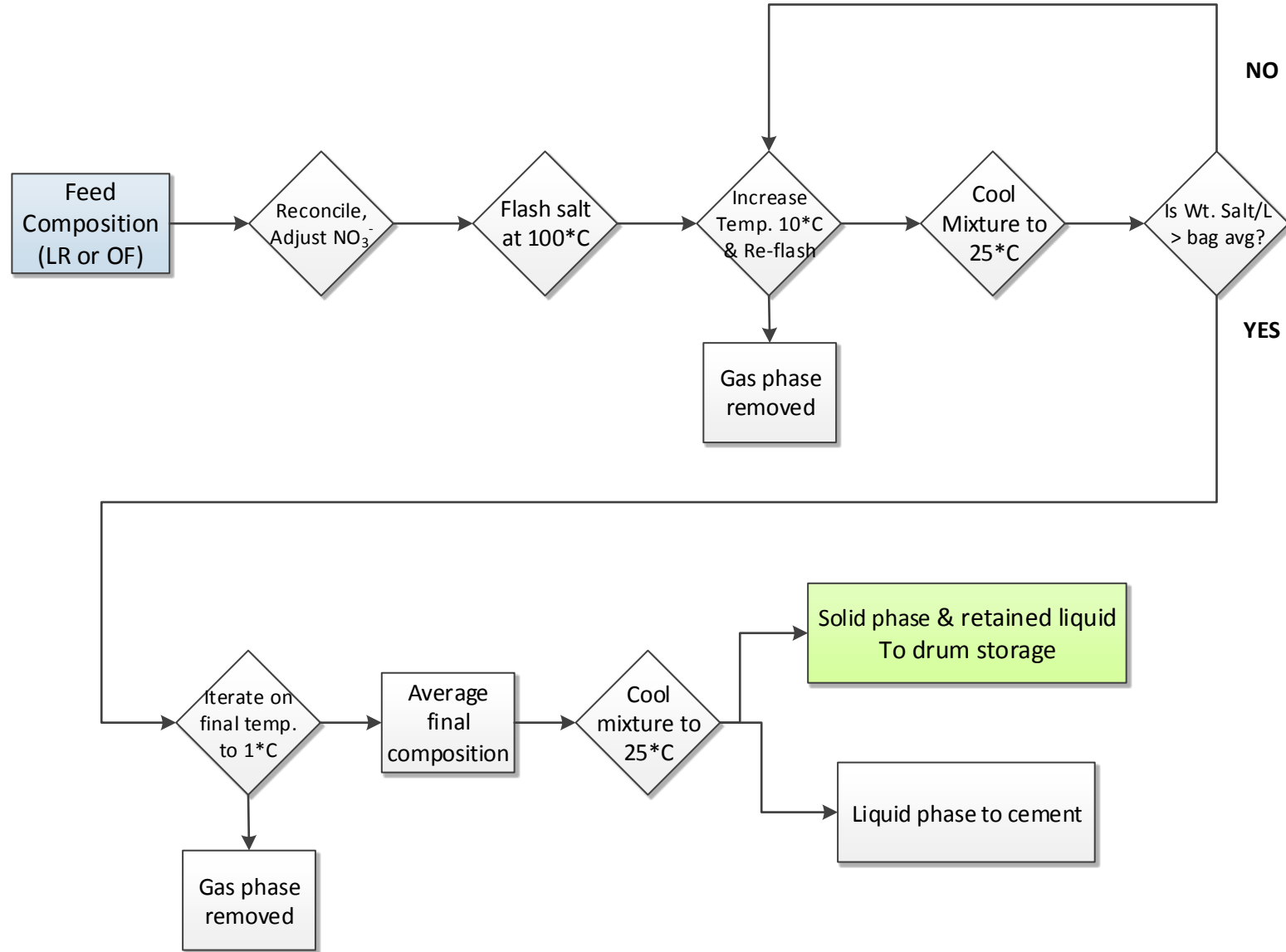


Figure 2. Modeling steps for generation of contents of parent drum.

The LR and OF feed streams to the parent drum are handled separately, but in a similar manner.

1. Solution compositions [1,2] were input into Stream Analyzer in g/L values. Since the Veazey analysis was taken during a time when TA-55 was processing high-chloride hydroxide cakes, higher amounts of stainless steel were probably introduced into the waste stream from corrosion of pipes and tanks. An attempt was made to reduce the amount to be more representative of the 1980 timeframe by reducing Fe, Cr and Ni as shown in Table 2.
2. The analysis was then reconciled to obtain charge neutrality. The amount of nitrate was increased for LR and reduced for OF.

Table 2. Adjustment to Stream Analyzer feed to reduce higher 304 SS content.

Species	Fe	Cr	Ni
Initial Analysis, g/L			
LR	17	3	1.8
OF	7.9	1.94	1.205
Final Input, g/L			
LR	6.8	0.2	0.3
OF	2.1	0.3	0.4

3. Continuous batch operation of the evaporator was modeled as a series of flash calculations to remove water and nitric acid. The initial acid concentration was estimated from the ion exchange procedures as 3.3 and 0.5 M HNO₃ for LR and OR, respectively. The flash temperature was increased in 10°C increments. After cooling the mixture to 25°C, the ratio of weight solid salt to volume saturated liquid was calculated and compared to ratios shown in Table 1.

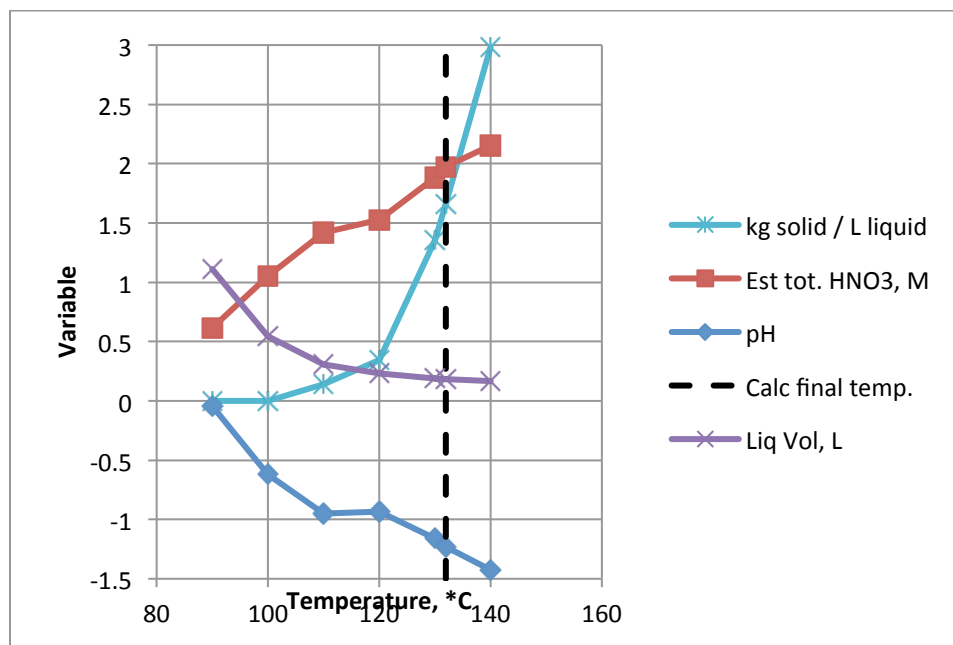


Figure 3. Mixture property changes for an Oxalate Filtrate mixture resulting from a series of flash calculations. The vapor phase is removed after each flash.

Figure 3 illustrates this process. A second series of cases were then run at 1 degree centigrade increments until the desired ratio was obtained.

4. The molecular output from Stream Analyzer provided input to an Excel spreadsheet (LR-OF Mix+liq) that converted the molar quantities into weight fractions of reagent chemicals that could be mixed to recreate the salt and liquid mixtures. Water (oxygen) and nitrate were conserved.
5. The quantity of saturated liquid retained by the solid crystals was calculated as follows. It was assumed from literature on sand-like mixtures that the empty space between the solid particles would occupy 30 percent of the total volume. In other words, the void fraction is 0.3. From knowledge of drainage curves from the petroleum industry, 50 percent of the void volume was estimated to remain liquid filled after gravity drainage. The procedure specifies that a vacuum was pulled through the salt crystals. Owing to the difficulty of disposing of the remaining liquid that was mixed with gypsum cement in one gallon cans, the operators at the time appear to have left as much liquid with the crystals as practical. The observed liquid after 30 years of Oswald ripening of the crystals may help support this observation.
6. The calculated volume of liquid is then added back to the solid phase and represents the feed stream to the parent drum.
7. Over 30 years, operators at WCRR reported that most of the salt bags decomposed and ruptured and deposited liquid onto the bottom of the drum. Calculations for drum 68660 indicate that LR and OF mixtures can produce another 2 liters of liquid. Since the liquid phase is acidic, the lead liner was probably attacked. (The WCRR operators reported decomposed lead liners in many of the drums.) Based upon experimental measurements by Ferris [5] and Hara [6], the maximum solubility of lead nitrate in 3 molar nitric acid was estimated at 15 wt. % lead nitrate in the liquid phase. We may assume that lead dissolved at the lead liner and produced a saturated solution of nitrate. One may then assume that lead nitrate diffused over the next 30 years into the bulk of liquid phase. An average lead nitrate concentration in the liquid phase may be calculated as follows. Based upon an analytical solution in Carslaw and Yeager [7],

$$D_{(\text{Pb}(\text{NO}_3)_2)} = 3\text{e-}11 \text{ m}^2/\text{sec}$$

$$D_{\text{eff}} = 0.3^2 * 3\text{e-}11 \text{ m}^2/\text{sec} = 1\text{e-}11 \text{ m}^2/\text{sec}$$

$$R (\text{drum}) = 0.279 \text{ m}$$

$$t = 30 \text{ years}$$

$$Dt/R^2 = 0.12$$

$$\text{From Carslaw and Yeager [6], Figure 12, } C_{\text{avg}}/C_{\text{wall}} = 0.65$$

Thus, the average concentration will be about 60% of the wall concentration or about 9 wt. % lead nitrate in the **liquid** phase. This corresponds to 2.2 wt. % in the total salt mixture.

The remaining calculation addresses the WCRR repackaging process to determine the composition and distribution of aqueous phase as free liquid and the amount retained with the solid salt.

4.2 Estimation of Sibling Drum Compositions

WCRR processing and the corresponding model steps are given in Figure 4.

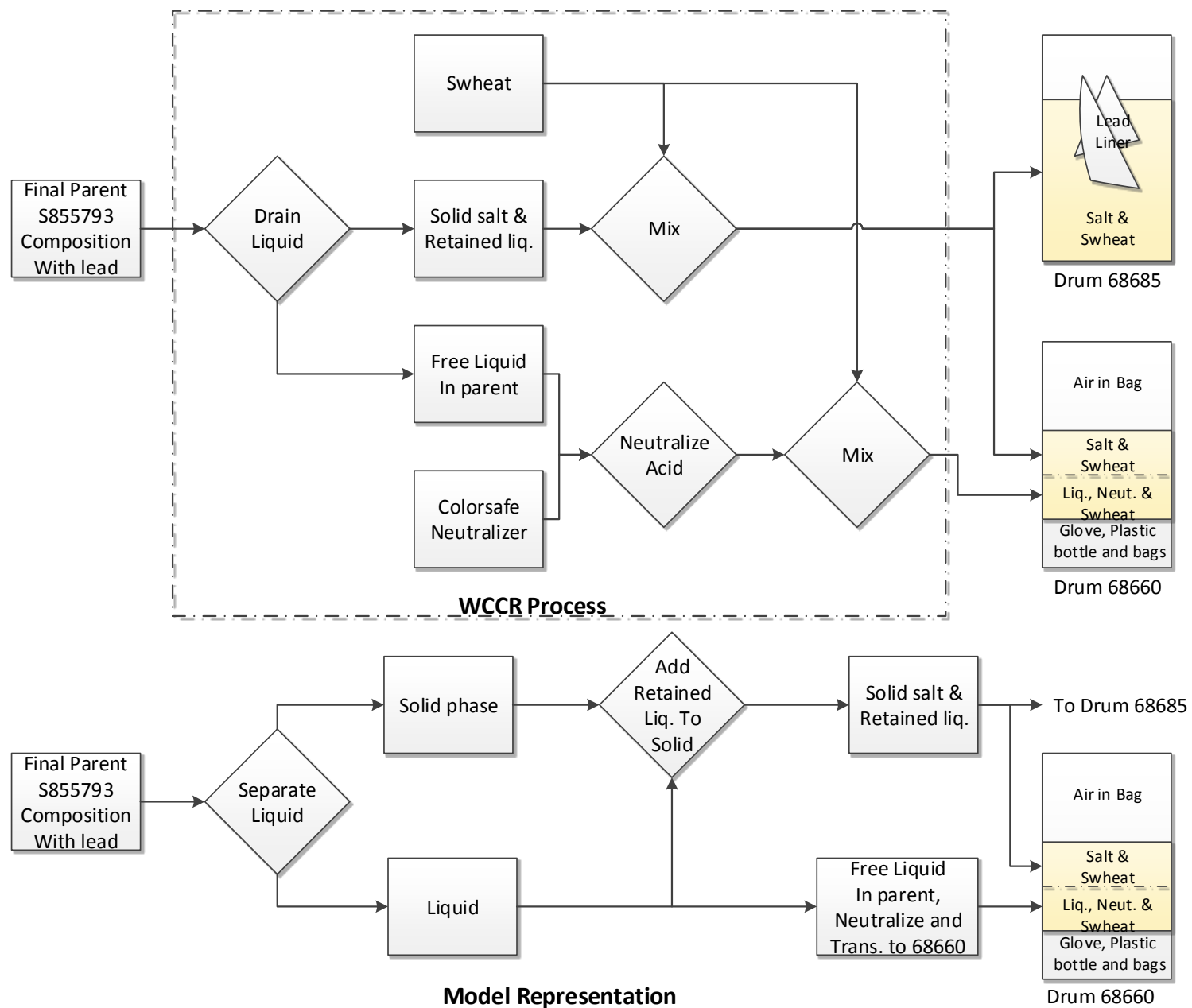


Figure 4. Representation of the WCCR operation by the Stream Analyzer model.

In this figure, processing and repackaging the contents of the parent drum by WCRR are represented schematically. A corresponding flow diagram for the modeling steps is also shown. In the actual process, retained liquid accompanies the solid salt crystals after the free liquid is drained and neutralized. The model, on the other hand, does a clean separation of liquid - then recombines all but the measured 2 gallons free liquid with the solid salt crystals.

Between Figure 2 and 4, lead nitrate is added as described in step 7 above. The WCRR operation is modeled by the following steps.

1. Model input consists of solid nitrate salts, entrained liquid from the separations in TA-55 and lead from dissolution of the lead liner that were introduced into the parent drum in 14 bags. A new solid / liquid equilibrium is calculated. The output is given in Table 4 and corresponds to 126 kg of salt plus about 2 kg of lead oxide.
2. The molar quantities are converted to reagent salts and listed as weights of free liquid and solid salt with retained liquid. The liquid retained with the solid is defined as the total aqueous phase minus the measured volume of free liquid. The total aqueous phase is dependent upon the initial assumptions in step 5 for the parent drum.

Table 3 lists the total composition for Drum 68660 of solid salt, retained liquid and free liquid. This mixture is expected to be wetter and less reactive than the solid salt, retained liquid and Swheat layer. Table 4 breaks down the distribution and lists the elemental weight percent of elements. It is noted that the 2 gallons nitrate liquids does not include Kolorsafe neutralizer that is included in Table 5.

Table 3. Total Composition of Contents, Drum 68660; Free liquid, Solid Salt & Retained Liquid

	Drum 68660	
	Free Liquid, Solid Salt & Ret. Liq.	
	Total Liq. & solid salts	Wt. fraction
	Kg	
Al(NO ₃) ₃ * 9 H ₂ O	1.8840	0.0447
Ca(NO ₃) ₂ * 4 H ₂ O	7.4909	0.1779
KNO ₃	0.0148	0.0004
Cr(NO ₃) ₃ * 9H ₂ O	0.0912	0.0022
Fe(NO ₃) ₃ * 9H ₂ O	2.8601	0.0679
H ₂ O-HNO ₃ -Al-Ca-Cr-Fe-Mg-Ni (O bal)	0.1593	0.0038
Mg(NO ₃) ₂ * 6H ₂ O	21.0214	0.4991
NaNO ₃	4.7659	0.1132
NaF	0.0000	0.0000
Ni(NO ₃) ₂ * 6H ₂ O	0.0104	0.0002
Pb(NO ₃) ₂	1.7159	0.0407
(COOH) ₂	1.2093	0.0287
KOH	0.8920	0.0212

Table 4. Composition Summary for WCRR Salt Handling

Parent Drum Composition						Drum 68660 Solid Salt and retained Liq.					68660 Free Liq. Layer		68660 Solid & Retained Liquid	
Input from Stream Analyzer LR+OF+2% wt Pb	Aque- ous	Solid	Wt.		Free Liq. Layer 68660	Solid Salts	Remain. Retained Liq.	Total			Wt Element	Element Wt %	Wt Element	Element Wt %
	mol	mol	kg		kg	kg	kg	kg			kg		kg	
Al ₂ O ₃	4.007		0.409	Al(NO ₃) ₃ * 9 H ₂ O	1.5112407	0.000	0.373	0.373		Al	0.109	0.759	0.027	0.024
Ca(NO ₃) ₂ * 4KNO ₃		0.144	0.082	Ca(NO ₃) ₂ * 4 H ₂ O	6.0020685	0.008	1.480	1.489		Ca	1.019	7.113	0.253	0.227
CaO	50.555		2.835	KNO ₃	0.0002592	0.014	0.000	0.015		K	0.499	3.483	0.129	0.115
Fe ₂ O ₃	2.707		0.432	Cr(NO ₃) ₃ * 9H ₂ O	0.0692612	0.005	0.017	0.022		Cr	0.009	0.063	0.003	0.003
H ₂ O	332.122		5.985	Fe(NO ₃) ₃ * 9H ₂ O	1.0996164	1.489	0.271	1.761		Fe	0.152	1.060	0.243	0.218
Mg(NO ₃) ₂ * 6H ₂ O		292.921	75.107	H ₂ O-HNO ₃ -Al-Ca-Cr-Fe- Mg-Ni (O bal)	0.1277485	0.000	0.032	0.032				0.000	0.000	0.000
MgO	14.264		0.575	Mg(NO ₃) ₂ * 6H ₂ O	1.8387698	18.729	0.454	19.183		Mg	0.174	1.217	1.818	1.631
NaNO ₃	14.293	188.927	17.273	HNO ₃	9.955E-07	0.000	0.000	0.000				0.000	0.000	0.000
Ni(NO ₃) ₂ .6H ₂ O		0.267	0.078	NaNO ₃	0.6107707	4.004	0.151	4.155		Na	0.165	1.154	1.124	1.009
NiO	0.000			NaF	0	0.000	0.000	0.000				0.000	0.000	0.000
(COOH) ₂	21.439		1.930	Ni(NO ₃) ₂ * 6H ₂ O	7.466E-06	0.010	0.000	0.010		Ni	0.000	0.000	0.004	0.004
PbO	8.266		1.845	Pb(NO ₃) ₂	1.3764137	0.000	0.339	0.339		Pb	0.861	6.012	0.212	0.191
Cr ₂ O ₃	0.172		0.026	(COOH) ₂	0.9700295	0.000	0.239	0.239		C	0.259	1.806	0.064	0.057
Cr(NO ₃) ₃ .9H ₂ O		0.049	0.020	KOH	0.7154963	0.000	0.176	0.176						
Fe(NO ₃) ₃ .9H ₂ O		14.783	5.972	NaOH	0	0.000	0.000	0.000						
HNO ₃	201.783		12.715											
KNO ₃	25.374		2.565	Total	14.322	24.261	3.532	27.793			3.246	22.668	3.877	3.478
NaF	5.507		0.231											
Total			128.096											

5.0 PREDICTED DRUM COMPOSITION

The parent and drum data sheets provide the necessary input for calculating the weight of salts in the parent drum and weight of “Inorganic Matrix” in the sibling drums. Calculation of the weight and volume of the salt layers in sibling drums is based upon the following input.

1. The OLI software estimates the densities of the saturated liquid and solid salts as 1.89 and 1.67 kg/L.
2. From the ion exchange process, the estimated acid content is 3.3 M HNO₃.
3. The WCRR data sheet indicates that 2 gallons of liquid were drained from the parent drum.
4. We assume that the free liquid and Kolersafe acid neutralizer are absorbed with a 3 to 1 ratio of Swheat to total free liquid after neutralization.
5. The density of Kolersafe is 1.09 kg/L.
6. The measured density of dry Swheat is 0.55 kg/L. Since it expands when wetted, the density was measured at 0.53 kg/L at a ratio of 3:1 Swheat / water by volume. The dry density, though not significantly different, was used in this calculation.

Based upon this input, the attached spreadsheet yielded Table 4. It provides an estimate of weight, volume and height of the neutralized liquid nitrate layer and nitrate solid layer. Interestingly, the independent volume measurement by RTR, agrees with the estimated total volume of the nitrate mixture layer within measurement error.

6.0 LIMITATIONS OF MODEL ANALYSIS

While performing the calculation procedure and during subsequent discussions, a number of anomalies became apparent in the analysis.

1. The amount of water in the saturated liquid appears to be too small. This observation corresponds to a higher density for the saturated liquid than the solid salt precipitate. While concentrations of saturated sodium nitrate and calcium nitrate binary salt solutions, reported in the literature, agreed very well with model predictions, the complex liquid mixtures reported here have densities greater than the solid crystal phase. It is thought that cation complexes with oxalic acid may increase cation solubility in these complex mixtures. OLI Systems discovered that aluminum nitrate does not have a value in the database for molar volume. This oversight oversight can lead to higher density calculation and is being corrected by OLI Systems.
2. Stream Analyzer does not have solid lead nitrate in the database. This is why no precipitate was predicted and literature was used to estimate lead nitrate solubility in the presence of nitric acid. Common ion effects from other nitrates may further lower the lead concentration.

In summary, the most significant impact of these anomalies is that the liquid fractions may include more water than estimated from the model. This difference will reduce the energetics and flame temperature of the reaction. If a more accurate water content is desired, the following procedure may be followed. This experimental procedure, in effect, adds back the excessive nitric acid that was removed during the flash vaporizations.

1. Construct a small scaled salt mixture given in Table 3.
2. Add one half the desired liquid phase as 3.3 M nitric acid. Heat to about 50°C to dissolve the salts and allow it to equilibrate. Additional liquid will be released from the hydrated crystals.

Higher temperatures are not recommended since it may cause premature reaction of oxalic acid at the higher acidity of the mixture.

3. Cool and gravity filter the remaining crystals.
4. Measure the weight of the solid crystals and retained liquid. Measure the volume of liquid.

Repeat steps 2 & 3 until:

$$\frac{\text{weight of solid salt crystals plus retained liquid, kg}}{\text{Volume of free liquid, gallons}} = \frac{27.5 \text{ kg}}{2 \text{ gallons}}$$

5. Use the ratio of salt mixture weight to added nitric acid to scale up the mixture.

This procedure only approximates the actual process but will not waste significant quantities of nitrate salts.

7.0 ALTERNATIVE ANALYSIS BASED UPON TA-55 PROCEDURES

Concurrent to development of these compositions, significant effort went into determining, from archived TA-55 procedures, an estimate of salt composition. Longmire et. al. [3] traced back from individual bag IDs the feed streams and some of the processes that created the waste salts. An estimate of salt composition for bags loaded into the parent drum was made. An estimate of which parent drum bags were loaded into drum 68660 was made from a comparison of isotopics of the bags and isotopics from air filters in WIPP. Details of this analysis and reactivity results can be reported in the future.

Table 5. Contents and estimated composition of the nitrate salt layers.

	Weight, Kg	Volume, Liters	Height, Inches		
Basis:					
Weights - in Kg					
Steel drum	27.7				
Plastic liner	2				
Fiberboard	3.7				
Total container weight	33.4				
Iron Based Metal/Alloys					
Other metals (lead liner)					
Rubber ("lead" glove)	5				
Plastic (waste)	6				
Inorganic matrix	71.6				
Total net contents	82.6				
Gross Wt	116				
Liquid Nitrate Layer					Wt. fract.
Nitrate Salt	14.3	7.6			0.351184
Average equiv. number nitrate salt bags	1.6				
Kolorsafe Neutralizer	5.5	5.1			0.136264
Swheat	20.9	38.0			0.512552
Total	40.7	50.6	8.9		1
Nitrate Solids Layer					
Nitrate Salt	23.8	14.2			0.769778
Average equiv. number nitrate salt bags	2.6				
Swheat	7.1	12.9			0.230222
Total	30.9	27.2	4.8		1
Total Nitrate Layer Height, in			13.7		
Estimated Nitrate Layer Height from RTR			14		
Volume estimate error, inches			0.3		

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