

PHYSICAL AND CHEMICAL ASPECTS OF THE DIRECT EVAPORATION OF INEEL SODIUM BEARING WASTE

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ABSTRACT

Solidification of simulated Idaho National Engineering and Environmental Laboratory (INEEL) radioactive liquid Sodium Bearing Waste (SBW) by processing through an evaporator was demonstrated [1, 2, 3]. Upon cooling, the bottoms solidify into a monolithic form that contains no free liquids as required for disposal as a transuranic (TRU) waste at the Waste Isolation Pilot Plant (WIPP). The evaporation process was demonstrated with the expected range of SBW simulant concentrations as well as with one batch of actual radioactive waste. Simulated tank heel solids were included in several of the SBW simulant tests. Pilot plant data was obtained from laboratory evaporators as well as from a scalable vertical agitated thin-film evaporator at a vendor site[4].

The evaporator process separates the water and nitric acid from the SBW by boiling at temperatures below 125°C. The concentrated bottoms material solidifies upon cooling. The off-gas and volatiles can be condensed for direct solidification as a mixed low-level waste or neutralized for recycle back through the evaporator. If the SBW bottoms product cannot be sent to WIPP, it would be temporarily stored and re-liquefied for conversion to an alternative disposal form at a later date.

This paper covers the results of a series of flask-scale, model-scale in-container, and pilot-scale agitated thin film evaporator tests. Reduced data from over 350 hours of testing and over 5500 separate analyses are summarized. The test objectives were to identify a range for the evaporator's operational parameters, to examine the physical process, and to find the partitioning factors of the volatile and semi-volatile waste species relative to the solid bottoms product and the vapor phase.

INTRODUCTION

As part of a legally binding Settlement Agreement between the Department of Energy (DOE) and the State of Idaho, the Tank Farm Facility (TFF) tanks at the INEEL are to be taken out of service by December 31, 2012 [5]. A major element of the TFF closure is the removal and treatment of 1,000,000 gallons of SBW contained in the tanks. SBW is a liquid, acidic radioactive waste with high concentrations of sodium and nitrate. Several options for SBW treatment are under consideration [6, 7] including direct evaporation (DE), an option recommended by the National Academy of Sciences [8].

The DE process results in a volume and mass reduction of the waste via evaporation. The concentrated evaporator bottoms then solidify upon cooling. This bottoms concentrate would be classified as remote-handled (RH) TRU waste, destined for direct disposal at the Waste Isolation Pilot Plant (WIPP). The DE bottoms product could also be stored for later conversion to another form if disposition in a deep geological repository is deemed necessary. Vapor overheads from the evaporation process would be condensed, concentrated in an available evaporator fractionator, neutralized, and grouted for disposal as a low-level waste (LLW) or the neutralized overheads concentrate could be recycled back to the feed to be included with the RH-TRU waste. Another possible scheme would scrub the acid and contaminants from the off-gas and recycle the neutralized scrub solution back to the feed to the DE process. The remaining essentially clean water vapor could be discharged to the environment after HEPA filtration.

Previous experimental work conducted in fiscal year (FY) 2002 demonstrated that the DE process was technically feasible for the specific composition of SBW in the INTEC tank WM-180, one of three 300,000-gallon capacity SBW tanks in the TFF [9]. Previous work also included a successful treatability test involving the DE of actual WM-180 SBW. DE experimental work has also been performed at other times in support of SBW pretreatment options, or as part of another treatment scenario [10, 11]. Experimental

work detailed in this report is a continuation of the work conducted in FY-2002, with emphasis placed on another TFF tank composition, WM-189, as well as on further understanding of the DE process control variables.

A total of 25 flask-scale evaporation test runs on WM-189 SBW simulant were conducted [12]. Six runs were performed at three different vacuum settings: 20, 15, and 10 in Hg. One run was specifically conducted to produce a crystal free liquid bottoms sample for viscosity measurement. Two test runs were conducted to determine the minimum bottoms concentration that would result in a solidified bottoms product and to collect sequenced condensate data. Two ambient pressure runs were conducted to determine the maximum concentration obtainable before visible NO₂ formed, and two runs were used to determine the highest vacuum allowable without producing undesired film boiling. Three test runs using partially neutralized feed were completed to determine the effect of SBW neutralization on the concentrated bottoms product. Six tests were completed to evaluate acid recycle effects on the concentrated bottoms product and the overheads composition. The last three test runs evaluated the composition of NO_x in the vapor.

The majority of testing was conducted under vacuum because of the imposed INEEL evaporator operating temperature limit of 125°C. This limited the operating vacuum to 10 in. Hg at the INEEL's ambient pressure (380 mm Hg absolute). The maximum temperature may be limited to about 130°C, because of the decomposition of aluminum nitrate. Testing demonstrated that boron, chloride, nitrate, and mercury are volatile when they are above 0.1 wt% in the SBW simulant feed (0.1 wt% of the feed mass of the constituent was collected in the condensate). Fluoride appears to be volatile but the analytical results obtained are very sporadic and in most cases no fluoride was detected. It was observed that refluxing, controlling the wall temperature, or limiting boiling time at high temperature can minimize semi-volatile species carry-over. Non-volatiles were present in the condensates at mass fractions of 1.0E-4.0 to 1.0E-6.0. The higher mass fraction values occurred in runs in which undesired film boiling occurred. Typically, less than 1.E-5.0 mass fraction of the non-volatiles are found in the overheads.

Overheads from the evaporation process are nearly 100% condensable at the "sub-cooled" condensing temperature of 5-10°C. A small amount of non-condensables may be formed, but since the quantity is small the process can be operated under vacuum with no vent. Three runs were performed during which there was no vent. For these runs, a small amount of non-condensable vapor was collected in a bag however, the amount was less than 0.03 wt% of the feed and some of this mass was gas displaced by condensate collection.

Overall, DE treatment of SBW, based on tank WM-189 and WM-180 simulant tests, is feasible and results in a monolithic form that is 18 to 33% (depending on the waste simulant and degree of boildown) of the original simulant feed volume. The tests also indicate that volatile and semi-volatile emissions can be minimized through condensate reflux, the recycle of neutralized condensate, and process control.

CONCEPT FUNDAMENTALS

The aluminum nitrate present in SBW forms hydrates that chemically bind up to nine water molecules for each aluminum nitrate molecule formed. Thus, an aluminum nitrate solution like SBW can be concentrated by evaporation to the extent that the entire solution turns solidifies upon cooling. Other metals, present in SBW, that significantly aid in binding water by the formation of hydrated nitrates or sulfates are: Ca, Fe, Mg, Mn, and Ni. Concentration, through evaporation, of the alkali metal nitrates in the presence of nitric acid form solid binary compounds such as KNO₃•HNO₃ and Na NO₃ •HNO₃. These compounds contribute to the formation of a solid product as well.

PROCESS FUNDAMENTALS

A flow diagram of the DE concept is presented in Fig. 1. As shown, SBW is fed to an evaporator, which produces a concentrated bottoms product and an overhead vapor. The concentrated bottoms product solidifies upon cooling and could be packaged for disposal as RH-TRU waste. Overhead vapor is sub-cooled and condensed for over 99.97 wt% recovery. The condensate is then sent to an existing evaporator-fractionator system where the acid and other contaminants are further concentrated and subsequently

neutralized with MgO. The neutralized, concentrated condensate could then be recycled by combining with the input feed stream to the evaporator. Alternatively, the concentrated condensate could be grouted for disposal as a mixed low-level waste. The majority of tests discussed in this report were based on this latter concept.

Another possible condensate recycle scheme would scrub the acid and contaminants from the off-gas and recycle the scrub solution back to the evaporator feed stream. The remaining water vapor and other gases are then discharged to the atmosphere after HEPA filtration. The advantage to either recycle scheme is that only one waste form is produced, reducing the amount of mixed low-level waste to be grouted. The disadvantage to recycle is an increase to the RH-TRU waste volume.

Several evaporator equipment types had been considered, including; kettle boilers, falling film evaporators, thermosyphon evaporators, forced circulation evaporators, wiped-film and thin-film evaporators, and in-canister evaporators. Of these evaporator types, the agitated thin-film evaporator is most applicable for the SBW evaporation process because its ability to handle the solids component of the SBW stream is considered superior to the others.

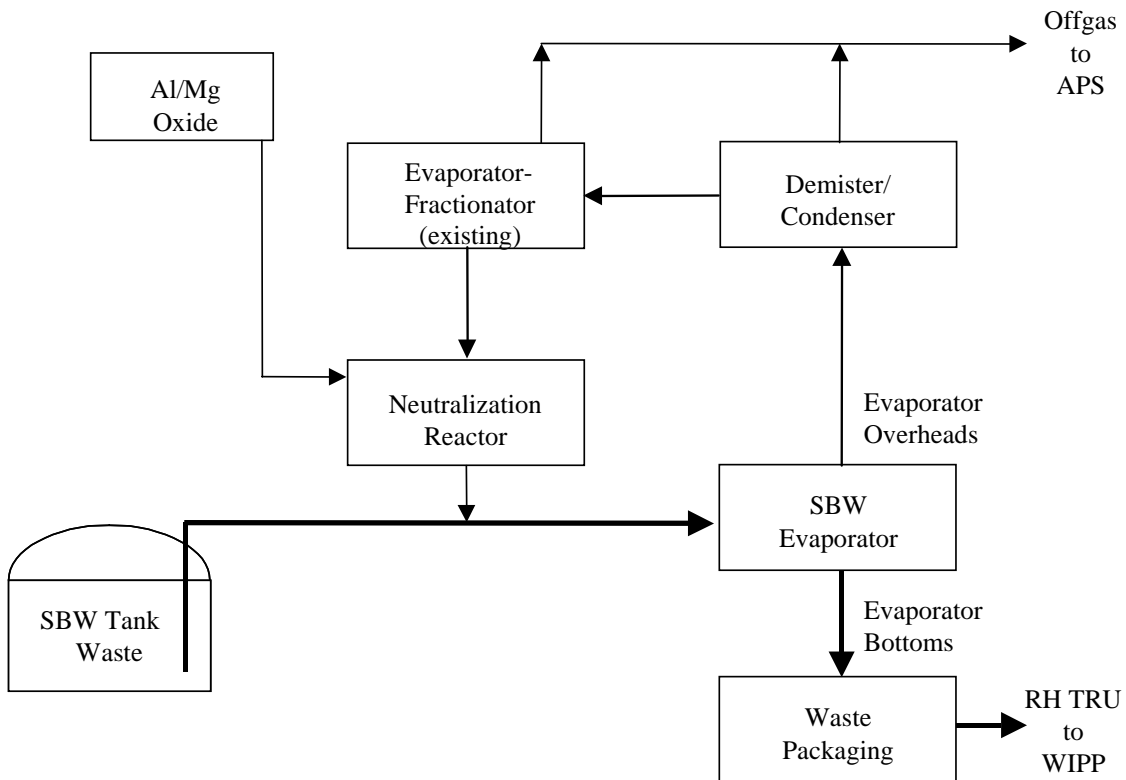


Fig. 1 Direct evaporation with overheads recycle block flow diagram

EXPERIMENTATION AND EXPERIMENTAL RESULTS

This paper covers a series of small flask-scale evaporation tests, model-scale in-container tests, and pilot-scale testing in an agitated thin film evaporator at LCI's vendor site. All experiments followed a similar flow and process pattern as previously outlined and included the following steps:

1. The liquid SBW simulant was transferred to an evaporator vessel: continuously, semi-continuously, or as a batch. At a temperature between 68 and 90°C, the liquid begins to boil, releasing its volatile constituents. The solution temperature increases, as the bottoms are concentrated.
2. Vapor exiting the evaporator vessel was condensed and collected at temperatures between 5 and 10°C (up to 30°C for the thin film evaporator tests). The mass of the collected condensate was determined and the solution sampled. For specific tests, condensate samples and masses were taken iteratively at a set time or at a set condensate to feed ratio.
3. Evaporator bottoms were removed, batch or continuously, to a collection/disposal container and allowed to cool and solidify. In the case of in-container evaporation, a pre-determined simulant volume was continuously fed at a rate determined by the amount of overheads collected. This was followed by further bottoms concentration until the desired final condensate to feed ratio was reached. The container was removed and cooled to solidify the bottoms. The solidified bottoms were then weighed and sampled.
4. Non-condensables leaving the condensate collection vessel passed through a secondary condensation system operated at 3-10°C. The off-gas exiting the second condenser was dried and the gas flow measured and vented or collected in a gasbag. Vacuum or gasbag pumps were used to maintain the desired system vacuum for those tests operated below ambient pressure. An off-gas analyzer was connected to the off-gas line to sample for nitrogen oxides (NO_x). An average concentration of 150 ppm for nitric oxide (NO) was determined from a model-scale run with no identified nitrogen dioxide (NO₂). The NO concentration peaked at 450 ppm when the bottoms were most concentrated. Less than 250 ml of gas was typically generated during flask-scale runs.
5. Temperatures were continuously monitored at various points for each test system.

The waste simulants selected for these tests were matched as closely to actual waste tank compositions [13, 14] as achievable. When it became apparent that little if any information could be gained by the addition of very small amounts of non-volatiles, these elements were not added. The simulant compositions for wastes residing in tanks WM-180 and WM-189 are shown in Table I.

Table I Tank WM-189 and WM-180 Compositions

Element	WM-189 Concentration	<i>M</i>	WM-180 Concentration	<i>M</i>
Aluminum	0.71		0.66	
Barium	6.00E-05		5.60E-05	
Boron	2.12E-02		1.20E-02	
Cadmium	3.91E-03		7.50E-04	
Calcium	7.33E-02		4.70E-02	
Cesium	3.00E-05		7.70E-06	
Chromium	5.63E-03		3.30E-04	
Cobalt	5.00E-05		1.90E-05	
Copper	9.50E-04		7.00E-04	
Iron	2.69E-02		2.20E-02	
Lead	1.16E-03		1.30E-03	
Magnesium	2.21E-02		1.40E-02	
Manganese	1.95E-02		1.40E-02	
Mercury	6.48E-03		2.00E-03	
Molybdenum	2.60E-04		1.90E-04	
Nickel	2.32E-03		1.50E-03	
Phosphorus	2.06E-03		1.40E-02	
Potassium	0.23		0.20	
Sodium	2.04		2.10	
Strontium	1.40E-04		1.20E-04	
Zinc	1.07E-03		1.00E-03	
Zirconium	3.60E-04		6.60E-05	
Chloride	2.06E-02		0.03	
Fluoride	1.64E-02		4.70E-02	
Nitrate	6.50		5.30	
Sulfate	0.11		7.00E-02	
Acid	2.86		1.01	

For the model-scale and pilot-scale thin film evaporator tests, RCRA metals and minor elements were not included in the simulant makeups. Chloride was not included for most of the thin film evaporator tests due to concerns of corrosive attack to pilot-scale equipment. No corrosion of the laboratory equipment was observed during any of the tests.

A summary of the runs from all of the evaporator tests is shown as Table II. With noted exceptions, each run in the table reports the nominal absolute operating pressure, the end point boiling temperature, the nominal volume reduction, the equivalent percent mass concentration (normalized to WM-189 feed simulate), the feed rate, and the wt% error in the mass balance.

Table II Run summary of selected direct evaporation experiments

Test Run #	Nominal Pressure, mm Hg	End Point Temp. of Solids, °C	Nominal Volume Reduction, %	Equivalent % Mass Concentration*	Feed Rate, kg/hr	Mass Balance, wt% Imbalance	Comments
FS-189-1	130	88.50	71.6	60.2	Batch	-0.102	
FS-189-3	260	111.50	72.7	61.1	Batch	-1.230	Mass loss during transfer
FS-189-4	260	111.50	72.7	62.6	Batch	0.041	
FS-189-5	380	120.50	72.2	61.9	Batch	-0.135	
FS-189-6	380	120.40	71.6	57.4	Batch	-0.289	
FS-189-8	380	112.50	66.0	50.1	Batch	-0.577	Lowest concentration for suitable product
FS-189-9	380	112.90	67.7	54.0	Batch	-0.221	
FS-189-10	640	132.30	70.0	56.7	Batch	-0.325	
FS-189-11	640	132.30	70.0	56.7	Batch	-0.750	
FS-189-12	Varying	124.20	72.5	58.7	Batch	-0.109	Pressure varied 260-480 mm Hg
FS-189-13	Varying	124.50	72.3	58.2	Batch	-0.422	Pressure varied 260-480 mm Hg
FS-180-15	30	112.20	81.8	68.5	Batch	-2.300	
MS-com-SD	260	129.00	81.9	56.1	1.9	0.640	Very dilute combination simulant used
MS-189-1	380	125.50	75.6	62.8	15.1	0.270	
MS-189-2	380	125.30	73.0	61.5	12.5	-0.210	
LCI-189-3	380	n.a.	n.a.	56.8	43.1	Dn Ob	End point temperature is not accurately obtainable at LCI because of equipment configuration
LCI-189-4	380	n.a.	n.a.	56.8	69.4	Dn Ob	
LCI-180-5	380	n.a.	n.a.	58.0	55.8	Dn Ob	
LCI-180-6	380	n.a.	n.a.	58.0	55.3	Dn Ob	
LCIS-189-2	380	n.a.	69.9	59.1	54.6	Dn Ob	LCIS – Solids were added to simulant-none-baseline
LCIS-189-6	380	n.a.	68.3	58.9	56.0	Dn Ob	4.76 wt% 2 micron silica
LCIS-189-9	380	n.a.	n.a.	58.7	56.2	Dn Ob	4.76 wt% 5 micron silica
LCIS-189-12	380	n.a.	n.a.	60.8	55.8	Dn Ob	4.76 wt% kaolin
LCIS-189-18	380	n.a.	n.a.	57.6	65.8	Dn Ob	Chloride run

*Equivalent concentration is based on WM-189 Tank equivalent composition of nitrate species as the starting point at 0% evaporation.

F – Flask-Scale

MS – Model-Scale

LCI – Thin Film Evaporator at Vendor Site (LCI)

n.a. – Not Available

Dn Ob – Data not directly obtainable without longer run duration because of equipment holdup

Vacuum was used to lower the boiling point to keep the bottoms end point temperature below 125-130°C. For WM-189 simulant, absolute pressures below 335 mm Hg resulted in film boiling at about 50 wt% bottoms concentration; a nominal 380 mm Hg was chosen for most operations. Lower pressures were used successfully for FS-180-15 and MS-com-Sd. The more viscous nature of the WM-189 simulant at lower boiling temperatures inhibited the use of lower pressures.

A normalization of the mass concentration achieved for each evaporation test was performed to provide for the equivalent percent mass evaporated. The equivalent mass adjustment was necessary to allow for direct comparisons between different simulants as well as for comparison of same formulation makeups with different concentrations from the target. Few test runs reached concentrations over 60 equivalent wt% and for all cases, water insolubles were identified in the bottoms product.

Since only two of the runs obtained mass imbalances over 1.0 wt%, accountability was excellent overall.

At equivalent concentration values between 57 and 64 wt%, a hard and tough bottoms product is formed. The product shown in Fig. 2 required partial sawing before it could be chiseled in half.



Fig. 2 Picture showing nature of flask-scale product (saw and chisel marks required for breaking in half).

Experimental results revealed that a liquid-free bottoms solid, a desired characteristic, is produced at evaporative concentrations above 50 wt%. For all WM-189 flask scale testing, the maximum concentration (SBW mass reduction) obtained was at 63 wt% with a volume reduction of 72.5%. A more desirable “rock hard” product is produced at evaporative concentrations above 57 wt%. Concentration factors greater than 65 wt%, although theoretically achievable, were not observed experimentally with the WM-189 SBW simulant.

Only a small amount of non-volatiles, less the 1/100,000 of the original mass for any constituent in the evaporator feed, makes it into the condensate. Therefore, the concentration of non-volatiles in the concentrated bottoms is directly proportional to the initial feed concentration and boil down ratio. The amount of transfer of the non-volatiles and the semi-volatiles to the condensate is greatly dependent on transfer by aerosols and carryover of mist. Properly designed condensate disengaging and reflux sections are therefore essential elements in a full-scale facility.

A key issue relative to SBW evaporation has to do with the fate of its volatile and semi-volatile components. Volatiles include mercury, chloride, boron, and nitrogen as nitric acid and reduced nitrogen oxide gases. Apparently the bulk of the nitrogen oxide gases, NO, NO₂, and N₂O react with or are absorbed by the sub-cooled condensate. This is discussed later in this section.

The factors affecting the quantity of volatiles and semi-volatiles released to the off-gas are, 1) the bottoms concentration, 2) the neutralization of the SBW-simulant feed, and 3) the amount of condensate reflux. The temperature is a factor but is related to the bottoms concentration. The primary factor in the transfer of volatile and semi-volatile constituents to the condensate is the bottoms concentration. Data on condensate levels of volatiles and semi-volatiles indicate that temperature and pressure have little effect.

Fig. 3 illustrates the acid partitioning from the feed to the condensate for 10 different test runs. At bottoms concentrations above 60 equivalent wt%, 80 wt% of the acid from the feed transfers to the condensate. At

higher bottoms concentrations, acid is generated from the reaction with water of aluminum and iron nitrate, as indicated by Eq. 1.

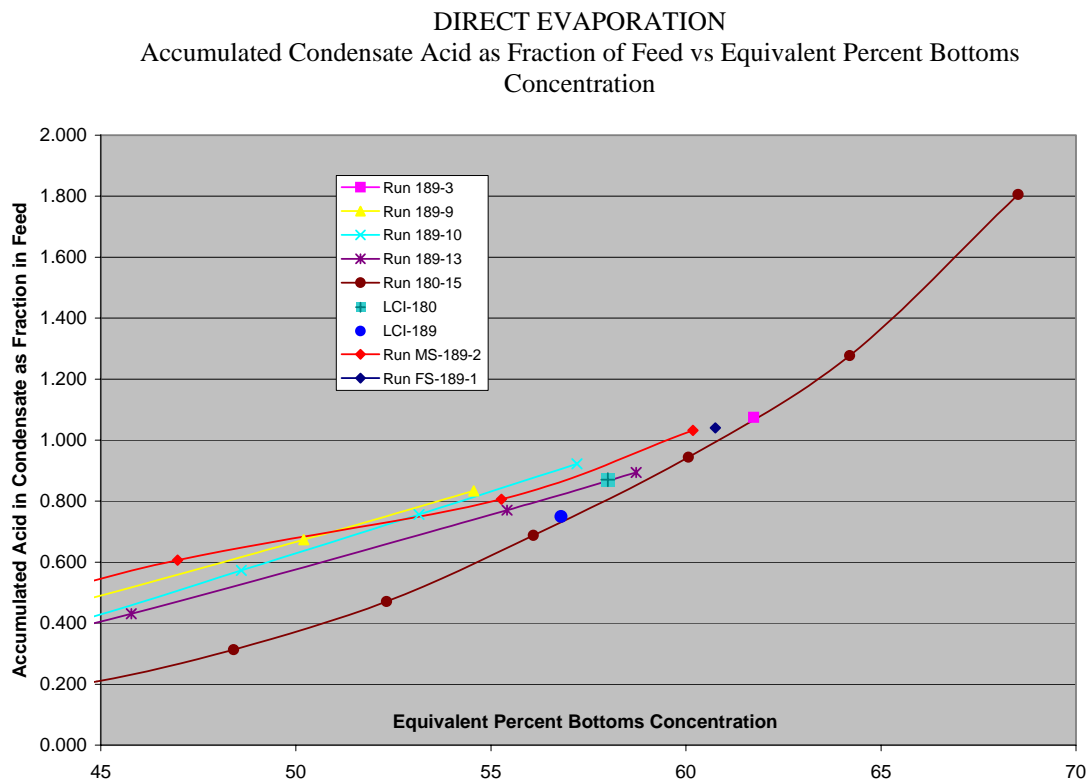


Fig. 3 Acid partitioning to condensate



If the feed contains little acid relative to the aluminum, then an even greater fraction of acid will be formed and volatilized to the condensate. Under these conditions, the Al and Fe form water insoluble compounds. As discussed later, Al and Fe insoluble compounds were found in the condensate when the accumulated acid fraction in the condensate exceeded 1.0.

After water and total acid, mercury and chloride are the next most volatile species. The accumulated fraction of feed found in the condensate for these species is shown for selected test runs in Fig. 4. Most of the chloride in the condensate is believed to have transferred as HCl and most of the mercury as HgCl₂, since both species are quite volatile at the DE operating conditions. The transfer of Hg to the condensate is less dependent on simulant waste type or temperature than is chloride. This difference is indicated by Hg's closer correlation to the equivalent bottoms concentration. Total chloride transfer to the condensate occurs early in the process as evidenced by the flattening of the curves as bottoms product concentration increases. This transfer occurs before the preferred product concentration is achieved, while the Hg transfer continues to increase above 60 wt% bottoms concentrations. For test run 180-15, the Cl transfer is obviously lower than the other runs. This can be explained by the fact that WM-180 tank waste contains about 1.0 M acid while WM-189 tank waste has over 2.8 M. This acid dependency on chloride volatility is an indication that the primary volatile species is HCl.

A fraction of the boron is also transferred to the condensate. The specie has not been identified but is suspected to be a form of boric acid since thermo chemical analysis shows a boric acid component in the overheads. However, the mass fraction transferred is generally less than 0.025 that in the feed.

As expected, the results of a X-ray diffraction (XRD) analysis on the solid evaporator bottoms product identified NaNO_3 and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ as the primary crystalline compounds. The solid evaporation bottoms produced by one test run had an additional crystalline component, aqua magnesium nitrate – $(\text{Mg}(\text{H}_2\text{O})_6)(\text{NO}_3)_2$, since the feed for that test run contained MgO used to partially neutralize the acid. MgO was chosen since magnesium nitrate has up to six waters of hydration per mole of acid neutralized compared to other neutralizing agents.

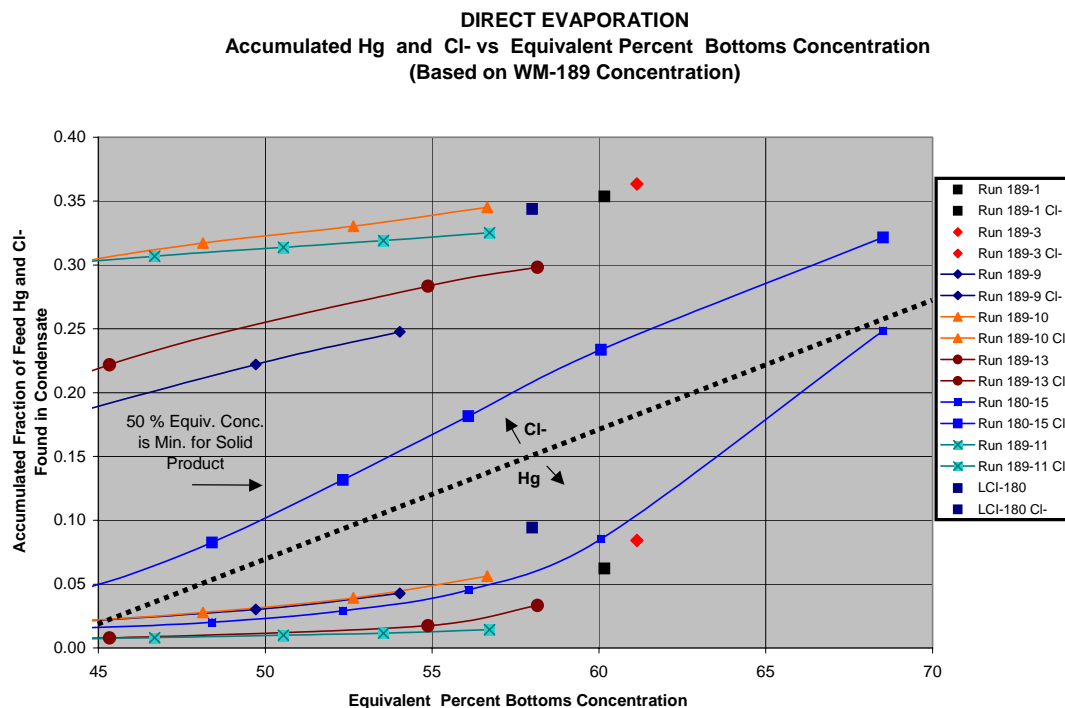


Fig. 4 Mercury and chloride partitioning to condensate

In the water insoluble portion of the bottoms product, XRD primarily found hydrated aluminum sulfates. These compounds included $\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$, $\text{Al}_6\text{O}_5(\text{SO}_4)_4 \cdot x\text{H}_2\text{O}$ and $\text{Na}_{0.58}\text{K}_{0.42}\text{Al}_3(\text{SO}_4)_2(\text{OH})_6$. Unlike the products of the WM-180 simulants, which had concentrations of water insoluble material from 4 to 7 wt%, the concentration of water insoluble compounds in the WM-189 simulant solid product was less than 0.4 wt% when the bottoms concentration was less than 60 wt%. At bottoms product concentration levels above 61 wt%, the insolubles component ranged from 2.8 to 5.1wt% in the model-scale tests. The formation of water insolubles also appears to be time dependant. The longer that a batch is at high temperature the more likely insolubles will form. This may be a result of some of the solution reaching a higher temperature than indicated by measurement or a result of the kinetics catching up to equilibrium.

The water insolubles have little effect on the bottoms product quality except to decrease nitrate and increase acid levels. However, if this effect continues to the extreme, the product changes consistency from “rock hard” to more clay-like. When there is not enough nitrates or water left for the higher hydrates to form, then, complete setup of the bottoms may not occur. Such was the case for runs FS-15 and FS-16, when the waste simulate feed solution was neutralized to less than 0.22 M acid with MgO .

In the laboratory flask-scale test apparatus, unwanted film boiling occurred at vacuums above 12 in Hg (approximately 330 mmHg absolute) when 50 wt % of the total condensate had been collected. The operating pressure required to achieve the 125°C maximum boiling temperature, and to prevent film

boiling, is about 390 mmHg absolute (10 in Hg at lab conditions). The onset of film boiling could be changed by increasing the heat transfer surface area, using a different heat transfer medium, or changing the method by which heat is imparted to the bottoms concentrate. For the thin film evaporator at LCI, film-boiling is not an issue because a faster evaporation rate can be obtained with a lower temperature difference.

Rhenium (Re) was added to the feed at 100 times the expected technetium (Tc) concentration to simulate this fission product. Depending on conditions, technetium is semi-volatile and may be released to the off-gas. However, no rhenium was found in any of the condensate samples, indicating its retention in the bottoms product. Re represents Tc well at high temperatures, but is inadequate at the low evaporator operating temperatures. Work with Tc in the simulant or in the actual waste is needed to assess how the Tc will actually partition in this process.

CONCLUSIONS

Overall test results indicate that DE treatment of radioactive SBW, based on SBW INTEC WM-189 and WM-180 tank simulants, is feasible and results in a solid monolithic waste-form that is approximately 18 to 33% of the original SBW volume. The waste volume reduction is approximately 50% with the neutralization recycling schemes.

Based on testing with SBW surrogates, DE results in a solid, liquid-free bottoms product over a reasonable range of process conditions. Experimental results reveal that a solid bottoms concentrate is produced at evaporative concentrations above 50 wt %. The maximum concentration obtained was at 68 wt% with a corresponding volume reduction of 82%. A desired “rock hard” bottoms product is produced at WM-189-simulant equivalent evaporative concentrations above 57 wt%. A hard product is also produced with the recycle flowsheets.

Controlling the wall temperature or limiting boiling time at high temperatures minimizes some volatile and semi-volatile species carryover. Volatile and semi-volatile constituents in the waste are mitigated through condensate reflux.

Results lead to the conclusion that off-gas volume is minimal after condensation at sub-cooled temperatures (12-20°C below ambient). The remaining vapor amount after condensation is less than 0.05 wt% of the overhead vapor leaving the evaporator. Visible NO₂ was observed in the evaporator flask at the end of the high temperature runs. However, there has been no visible NO₂ or detection of it by the NO_x analyzer downstream of the condensate collection vessel. In later tests, N₂O was determined to be the major nitrogen oxide gas at an indicated concentration of up to 20-volume %. An average value of 150 ppm NO was obtained from the model-scale tests under normal operation. A peak concentration of 450 ppm was reached when the evaporation endpoint was extended to a 61.5 wt% equivalent bottoms concentration. In contrast, high temperature offgas operations produced an average of 240 ppm NO without any detected NO₂.

Efforts to date have found that monitoring temperature in combination with the absolute pressure is not an exact indicator of evaporation completion since changes in the bottoms solution composition caused by the precipitation of nitrates changes the boiling point. This effect occurs randomly depending on the kinetics of the crystal formation. As such, the best process control method is to monitor and adjust the condensate to feed mass ratio. Even though bottoms temperature at a given pressure is an indicator of close arrival to the evaporative end point, continuous tracking of the condensate to feed mass ratio makes end point control exact. Such a control technique is common practice for evaporation in industry.

Recent examination of long-term storage effects shows differences can occur to the bottoms products. The products containing more water insolubles indicate higher deliquescence (water absorption) while the “rock hard” products appear to be more stable. There is, however no water solution leakage or separation from the product unless water is absorbed from the atmosphere. No weight gain in the product is evident when the relative humidity is less than 40%. Adding silica gel to the storage container on top of the product can mitigate the absorption of water¹. Off-gassing of the product continues for some period after setup.

Sampling has indicated that the gas is similar to what is released during evaporation with the detected nitrogen oxides being NO and N₂O. If the container is vented the evidence of any emission will tend to disappear after about six weeks.

Further work must be performed to quantify the effects of mist elimination and condensate reflux on final condensate volumes and properties. Experimental equipment used to determine these effects must be large enough to ensure that scale-up to the proposed SBW design treatment throughput is achieved. If one of the recycle schemes is employed then the need for this information may not be needed.

Additional tests with actual “hot” SBW in traditional treatability study format would determine the fate of cesium, technetium, and other radionuclides.

REFERENCES

- 1 J. A. McCray, L. G. Olson, S. J. Losinski, “Investigation of Direct Evaporation and Fractional Crystallization Technologies for Sodium-Bearing Waste Treatment,” Report INEEL/EXT-02-01043, September 2002.
- 2 R. J. Kirkham, Lockheed Martin Idaho Technologies Company, Internal Correspondence RJK-6-98 to W. H. Landman, “Sodium Bearing Waste Solidification By Evaporation,” dated September 29, 1998.
- 3 J. A. McCray, Westinghouse Idaho Nuclear Co. Inc. Internal Correspondence, JAM-11-94 to D. V. Croson, “Report on Freeze Crystallization and Evaporation/Precipitation Testing for Sodium-Bearing Waste treatment,” dated September 30, 1994.
- 4 D.L. Griffith, L.G. Olson, “Testing an Agitated Thin Film Evaporator for Solidifying a Mixture of Simulated Sodium Bearing Waste and Undissolved Solids (Test Series 2),” INEEL/EXT-03-01189, November 2003.
- 5 DOE, 1995 Consent Order and Settlement Agreement Between DOE and the State of Idaho Regarding Spent Fuel and Nuclear Waste Issues, October 17, 1995.
- 6 Engineering Design File 2373, “Process Design of SBW Treatment-Alternatives,” INEEL Project File No. 22681 Rev. 0, September 2002.
- 7 R. R. Kimmitt, Engineering Design File 2524 (DRAFT), “Feasibility Study of Direct Evaporation of Sodium Bearing Waste,” October 2002.
- 8 Governing Board of the National Research Council, National Academy of Sciences, Sponsored by DOE “Alternative High-Level Waste Treatments at the Idaho National Engineering and Environmental Laboratory, Ch12-What Should Be Done: Sodium-Bearing Waste” pp102, National Academy Press 1999.
- 9 J. A. McCray, L. G. Olson, S. J. Losinski, “Investigation of Direct Evaporation and Fractional Crystallization Technologies for Sodium-Bearing Waste Treatment,” Report INEEL/EXT-02-01043, September 2002.
- 10 J. A. McCray, Westinghouse Idaho Nuclear Co. Inc. Internal Correspondence, JAM-11-94 to D. V. Croson, “Report on Freeze Crystallization and Evaporation/Precipitation Testing for Sodium-Bearing Waste treatment,” dated September 30, 1994.
- 11 R. J. Kirkham, Lockheed Martin Idaho Technologies Company, Internal Correspondence RJK-6-98 to W. H. Landman, “Sodium Bearing Waste Solidification By Evaporation,” dated September 29, 1998.

- 12 R. J. Kirkham, Test Plan For The Laboratory Flask Scale Direct Evaporation Treatment of SBW, December 2002.
- 13 T. A. Batchellor and D. D. Taylor, "Characterization of Tank WM-189 Sodium Bearing Waste at the Idaho Nuclear Technology and Engineering Center," Report INEEL/EXT-02-01171, September 2002.
- 14 J. D. Christian, "Composition and Simulation of Tank WM-180 Sodium-Bearing Waste at the Idaho Nuclear Technology and Engineering Center," Report INEEL/EXT-2001-00600, May 2001.