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7. Abstract <p>This study identified and investigated techniques of selectively purging chlorides from the low-level waste (LLW) vittrification process with the purge stream acceptable for burial on the Hanford Site.</p> <p>Chlorides will be present in high concentration in several individual feeds to the LLW Vittrification Plant. The chlorides are highly volatile in combustion type melters and are readily absorbed by wet scrubbing of the melter offgas. The Tank Waste Remediation System (TWRS) process flow sheets show that the resulting chloride rich scrub solution is recycled back to the melter. The chlorides must be purged from the recycle loop to prevent the buildup of excessively high chloride concentrations.</p> <p>This report was prepared by Fluor Daniel, Inc., as part of the LLW Program.</p>		
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CHLORIDE REMOVAL FROM VITRIFICATION OFFGAS

May 1995

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For Westinghouse Hanford Company
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LIST OF TERMS

LLW	Low-level waste
MOG	Melter offgas
TWRS	Tank Waste Remediation System
WRAP	Waste Receiving and Packaging

CHLORIDE REMOVAL FROM VITRIFICATION OFFGAS

1.0 OBJECTIVE

The main objective of this study is to identify and investigate techniques of selectively purging chlorides from the low-level waste (LLW) vitrification process. The purge stream must be acceptable for burial on the Hanford Site.

Chlorides will be present in high concentration in several individual feeds to the LLW Vitrification Plant. The chlorides are highly volatile in combustion type melter and are readily absorbed by wet scrubbing of the melter offgas. The Tank Waste Remediation System (TWRS) process flow sheets show that the resulting chloride rich scrub solution is recycled back to the melter. The chlorides must be purged from the recycle loop to prevent the buildup of excessively high chloride concentrations.

Three alternate techniques have been considered for chloride purge. The techniques are:

1. Distillation
2. Chlorides precipitation
3. Ion exchange.

The technique selected must be selective for chlorides in order to minimize the volume of the associated non-vitreous purge stream. The chemical composition of this purge must be compatible with its incorporation into grout or some other solid, which will be sent to Waste Receiving and Packaging (WRAP) for disposal. The solidification operation will be housed inside the vitrification facility.

Only options which are found to be viable upon initial examination are developed into process flow sheets, facility layouts, and cost estimates.

2.0 SUMMARY

Based on the anticipated operating conditions of the LLW combustion melter, volatilities of various chemical species in the melter feed have been estimated, and are listed in Attachment 1. These estimates indicate that virtually all of the melter feed species, except SO_4 , NO_x , iodide and chloride, can be accommodated in the LLW product glass by recapturing the volatilized fraction from the melter offgas (MOG) and recycling it to the melter. The SO_4 and the NO_x will be converted into gaseous species that will exit the process recycle loop. Similarly iodide, which will approach 100 percent volatility in the LLW melter, will either be converted to a gaseous form that will exit the plant stack or report at very low concentrations to the glass. Because of these two mechanisms, and the very low concentrations of iodide expected in the vitrification feed, iodide purge is not expected to be a problem.

Chlorides, on the other hand, are unique in not now having a mechanism by which they can be purged to a plant effluent stream. They are both highly volatile in the melter, and readily absorbed by wet scrubbing in the melter offgas system. Some of the plant feeds will also contain high concentrations of chlorides. Therefore, the main task of this study is to identify and investigate techniques of selectively purging chlorides from the vitrification plant process recycle loop in a decontaminated, non-vitreous form.

The three chloride purge techniques which were investigated are distillation, precipitation, and Ion Exchange. Of the three techniques, only Distillation was determined to be technically feasible at the present time. The Chlorides Precipitation technique was determined to be far too complex and to have too many unresolved technical issues to be a viable option. The Ion Exchange technique would require a research and development program to produce a chloride-specific resin, similar to the fluoride-specific absorbent already under development. If such a resin could be commercialized, it may make Ion Exchange the simplest and most cost effective approach. At the present time, however, chlorides removal by Ion Exchange has not yet been successfully demonstrated. An alternate Ion Exchange technique would be to selectively remove dissolved radionuclides to permit the purge of the decontaminated effluent stream. In addition to chlorides, this approach would also purge fluorides, nitrates, phosphates and sulfates, causing an unacceptable increase grout production. For the above reasons, capital cost and facility configuration impacts are developed only for the Distillation alternative.

A comparison summary for the three chloride purge techniques is presented in the following table. The points of comparison are discussed in detail in Section 5.3.

Table 1. Summary of Chloride Purge Techniques.

	Distillation	Precipitation	Ion exchange
Technical feasibility	Probably feasible but resolution of uncertainties by further study or testing is needed.	Not viable because of excessive complexity, cost, technical uncertainties, and potential contamination of purge steam.	Not now viable because a chloride-specific ion exchange resin does not exist.
Facility design impacts	Add new grout room and lengthen melter cut-up cell. Total increase in floor space, approximately 440 m ² .	Not addressed.	Not addressed.
Operability/complexity	Should have acceptable operability and complexity.	Excessive complexity.	If a suitable resin could be developed, it may offer the best operability and minimum complexity.
Maintainability	Should be acceptable.	Higher maintenance requirements than distillation.	Process not yet commercialized so this issue was not addressed.
Maturity of technology	Technology of required unit operations is mature and available; however, laboratory or pilot-scale testing needed to reliably predict performance.	Chloride precipitation technology available. Technology to recover reagent needs development.	A chloride-specific ion exchange resin would have to be developed and tested.
Schedule impacts	Confirmatory design data would have to be developed by testing in a timely manner.	Issue not addressed because process is not viable.	Approximately 2 to 2-1/2 years required to develop a suitable ion exchange resin.
Regulatory impacts	Not a discriminating issue.	Not a discriminating issue.	Not a discriminating issue.
Safety	Should be compatible with safe plant design.	Should be compatible with safe plant design.	Should be compatible with safe plant design.
Cost TEC: Operating Cost:	\$57,010,000 \$8,260,000/yr.	Not developed	Not developed

3.0 TECHNICAL FINDINGS AND CONCLUSIONS

The following observations are made as a result of this study.

1. Chlorides purge by Distillation appears to be technically feasible, although fairly complex. The unit operations incorporated in this alternative are well known, and pilot scale operation can be readily carried out to resolve any design uncertainties. The areas of uncertainty are discussed in Section 5.2.
2. Chlorides Precipitation is not a viable chlorides purge technique. This is because of,
 - (a) the high cost of the chloride precipitation reagent, silver nitrate (AgNO_3),
 - (b) the potential contamination of the chlorides purge stream with residual silver compounds,
 - (c) the potential addition of silver to the LLW product glass,
 - (d) the potential contamination of the chlorides purge stream with radionuclides due to their interaction with the chloride precipitating agent,
 - (e) the overall complexity of the process.
3. A chloride-specific ion exchange resin is not, at present, commercially available. However, recent progress in developing a similar fluoride-specific resin suggests the realistic possibility that a chloride-specific, regenerable material could also be produced.

The future availability of a chloride-specific resin may possibly make the Ion Exchange alternative technically and economically feasible. Further study would be required to verify the feasibility.

4.0 DESCRIPTION OF ALTERNATIVES

4.1 DISTILLATION

For the following discussion, refer to the Distillation PFD (Attachment 2), the Distillation Equipment List (Attachment 3), the Distillation Utility Summary (Attachment 4), and the Facility Layout Drawings (Attachment 6). The reader should also refer to the TWRS PFD for Combined Pretreatment/200 MT/day LLW Vitrification Facility (Case 4C), which is not attached.

The Distillation option calls for filtration of the continuously-generated scrub solution purges from the two trains of the Melter Offgas System. This requires the addition of two parallel Scrub Filters (F-621 A&B) to the top of the existing LLW Scrub Filter Tank (TK-611). The accumulated filter cakes are periodically backflushed into this tank, while the filtrates are combined into a single stream that exits the MOG System.

The combined filtrate stream then enters the new Chlorides Purge System at a rate of 0.146 m³/min (38.6 gpm). This stream is first concentrated by about a factor of 10 as it passes through the Evaporator (EV-01). The disposition of the resulting overhead condensate will depend on its composition. If clean and free of dissolved semi-volatiles, this liquid may be purged to the existing Process Condensate Recycle Tanks (TK-800 A,B,C). However, a preliminary computer modelling of the evaporator predicts the loss of 40 to 50 percent of the incoming fluoride, and lesser amounts of chloride and nitrate, to the overhead condensate. Avoiding contamination of TK-800 A,B,C would require either,

- (f) the addition of a reflux column to re-absorb semi-volatiles from the evaporator overhead vapor (this method has not been demonstrated), or
- (g) diversion of the overhead condensate back to the Feed Preparation System where the condensate is re-evaporated.

The hot Evaporator bottoms are continuously transferred to the Distillation Feed Tank (TK-03) at a rate of about 0.017 m³/min (4.5 gpm). There, it is continuously blended with concentrated (92.5 percent) nitric acid, added at a rate of 0.017 m³/min (4.47 gpm). The resulting mixture, which contains 56 to 57 percent HNO₃, is cooled to about 65°C (150°F) to permit the continuous operation of a transfer pump. The pump discharge stream is warmed to 99°C (210°F) inside the Preheater (EC-05) before entering the top of the HCl Stripping Column (T-06).

The presence of high concentration's of nitric acid in the column feed permits the combination of ionic H⁺ and Cl⁻ to form molecular HCl (hydrochloric acid), which is somewhat volatile. Inside the HCl Stripping Column, the acidified feed falls through two packed beds, counter-current to the rising water and nitric acid vapors generated by the Reboiler (EC-07). These vapors volatilize HCl and HF from the descending liquid.

The other chemical species and radionuclides should remain non-volatile under these conditions because of their higher atomic weights and/or their presence in ionic, as opposed to molecular, form. The column bottoms stream should therefore retain these species as it gravity drains to the Recycle Neutralization Tank (TK-21), where it is cooled and neutralized. To the extent possible, calcium hydroxide ($\text{Ca}(\text{OH})_2$) and lithium hydroxide (LiOH) are used for neutralization rather than sodium hydroxide (NaOH). This is to avoid or minimize any increase in glass production. Ideally, the calcium and lithium added in the course of neutralization should be completely offset by corresponding reductions in the CaO and Li_2O content of the dry glass former stream.

The overhead vapor from the HCl Stripping Column contains water, nitric acid, HCl and HF . This stream is routed to the bottom of the adjacent HCl Rectifying Column (T-10), where a significant fraction of the nitric acid is condensed by counter-current contact with the descending reflux stream. The bottoms from the HCl Rectifying Column falls directly into the HCl Distillation Tank (TK-08). From there it is pumped back to the top of the HCl Stripping Column where it mixes with the incoming feed. The need for separate stripping and rectifying columns is based on equipment height limitations inside the hot cell.

The overhead vapor from the HCl Rectifying Column is partially condensed as it passes through the Condenser (EC-11). The resulting acidic condensate is separated in the HCl Overhead Accumulator (TK-12) from which it drains by gravity and is returned to the column as reflux. The remaining vapor, containing water, HCl , HF and a much reduced level of HNO_3 , passes overhead and enters the middle of the HF Stripping Column (T-13). This final column separates the HF from the HCl by distillation. Most of the more volatile HF is driven overhead as vapor. After total condensation in the Condenser (EC-15), the resulting aqueous solution of HF is sent to the HF Overhead Accumulator (TK-16). From there, a portion of the liquid gravity drains back to the column as reflux, while the remaining net overhead product is sent to the Recycle Neutralization Tank (TK-21) where it joins the bottoms from the HCl Stripping Column.

The HCl Stripping Column will definitely contain radionuclide contamination. The downstream HCl Rectifying Column and the HF Stripping Column may also contain radionuclides, either as a result of volatilization or upset entrainment from the lead column. Therefore, design conservatism places all three of these columns and their appurtenant equipment in a shielded process cell, rather than in a contact maintained area.

In a shielded process cell, remote process connections cannot be relied on to remain leak proof and tight in pressurized service. In this particular application, outleakage would be especially undesirable because it would release both acidic vapors and radionuclide contaminants into the cell air. It is therefore, proposed that the three columns operate at a slightly negative gauge pressure. The required partial vacuum is created by a Blower (M-17) continuously drawing suction on the vapor space of the HF Overhead Accumulator (TK-16). The gases drawn through the Blower will be a mixture of process non-condensibles and in-leakage air. The Blower discharge will tie into the quenched melter offgas streams

entering the existing LLW Venturi Scrubbers (SC-615A&B). This should permit the re-absorption of any acid gases present.

The aqueous bottoms from the HF Stripping Column contains most of the chloride in the form of HCl, a comparable mass rate of HF, and a much smaller amount of nitric acid. This hot liquid gravity drains to one of the two parallel-operated Chlorides Purge Neutralization Tanks (TK-18A&B). There, the acidic chlorides purge is cooled, sampled, and analyzed for residual radionuclide contamination.

Then, calcium hydroxide is added in order to precipitate the fluoride as calcium fluoride [if caustic soda were used, the soluble sodium fluoride would act as a retardant to the setting of the cement during the grout forming operation, which is discussed below]. The end point is determined by a fluoride electrode. Caustic soda is then added to raise the pH to above 7, but no higher than 12. The stream is then pumped to the Grout Feed Evaporator (EV-23), where it is concentrated to a 5 M solution, based on sodium, by driving off excess water. The stream is then gravity drained to the Grout Feed Tank (TK-27), where it is cooled to 32°C, before being mixed with grout formers inside 55-gal drums. The overhead from the evaporator is sent through the Condenser (EC-25) to the Process Condensate Recycle Tanks (TK-800A,B,C).

- Grout Forming

The entire batch process is performed in carbon steel drums with a 20 mil high density polypropylene liner (these liners are good to 110°C). The following steps will be performed:

1. An agitator and cooling coil is inserted into the drum.
2. The proper amount of feed (based on the 35 percent increase in volume) is charged into the drum.
3. A 50/50 mixture of cement and flyash is added in an amount equal to the weight of the feed.
4. The mixture is agitated until it is thoroughly mixed.
5. The agitator and cooling coil is removed and inserted into the next drum.
6. The drum is closed and is immediately moved to temporary storage for initial curing.

After initial curing of the grout is complete (about three weeks), the drums are removed from the vitrification facility and sent to an appropriate disposal site.

Based on a peak LLW vitrification rate of 200 megagrams per day, a maximum grout production rate of 12 drums per day is calculated. The total grout production is 28,000

drums containing 700 megagrams of chloride. This is an average of 2,000 drums per year for the 14-year campaign.

4.2 PRECIPITATION

For the following discussion, refer to the Precipitation PFD (Attachment 5) and the TWRS PFD for Case 4C, which is not attached.

The Precipitation option calls for filtration of the continuously generated scrub solution purges from the two trains of the MOG system. This requires the addition of two parallel Scrub Filters (F-621 A&B) to the top of the existing LLW Scrub Filter Tank (TK-611). The accumulated filter cakes are periodically backflushed into this tank, while the filtrates are combined into a single stream that exits the MOG system.

The combined filtrate stream then enters the new Chlorides Purge System. This stream is first concentrated in an evaporator. The excess water rejected overhead is condensed and sent on to the existing Process Condensate Recycle Tanks (TK-800A,B,C). The hot, concentrated bottoms stream is continuously transferred to the Iodide Precipitation Tank. There, nitric acid and a sufficient amount of silver nitrate are added to react with all the fluoride, chloride and iodide. Silver fluoride and silver chloride are soluble in the acidic solution. Only silver iodide is insoluble in the acidic solution. The silver iodide precipitate is removed by filtration and is recycled to the LLW Feed Preparation System.

The filtrate from the AgI Filter is sent to the Chloride Precipitation Tank where sodium hydroxide is added to neutralize the solution. Because of its low solubility in neutral solution, most of the AgCl precipitates. The contents of this tank are sent to the first AgCl Filter, from which clear filtrate containing dissolved AgF and AgNO₃ is routed to the Fluoride Precipitation Tank. Meanwhile, the AgCl filter cake is backflushed to the AgCl Wash Tank. Clean wash water is added to this tank to remove any dissolved radionuclides that may have been carried by the damp filter cake.

The resulting aqueous slurry is then sent to the second AgCl Filter. The contaminant-bearing filtrate is returned to the LLW Feed Preparation System, while the filter cake is discharged to the Silver Recovery Unit.

In the Silver Recovery unit, powdered aluminum is added to react with AgCl to form aluminum (III) chloride (AlCl₃), and elemental silver (Ag). The AlCl₃ is incorporated into grout or a similar waste form. The recovered silver is sent to the Silver Nitrate Production unit.

The filtrate from the first AgCl Filter undergoes several process steps to recover silver from dissolved species. This stream first enters the Fluoride Precipitation Tank where calcium hydroxide (Ca(OH)₂) is added as a reagent. This causes the conversion of soluble AgF to insoluble calcium fluoride (CaF₂). These newly formed solids are removed by the

CaF₂ Filter, and subsequently backflushed to LLW Feed Preparation. A slipstream of the filtrate, containing dissolved silver ions, is sent to the Iodide Precipitation Tank.

Most of the filtrate proceeds on to the Ag₂SO₄ Precipitation Tank. There, sulfuric acid is added to precipitate silver sulfate (Ag₂SO₄), which can then be filtered from the rest of the radionuclide containing solution. The filtrate, which contains volatile radionuclides, is recycled back to the LLW Feed Preparation System. Silver is recovered from Ag₂SO₄ in the Ag₂SO₄ Reduction unit by reaction with a reducing agent. The specific reducing agent to be used has not yet been determined. However, literature research reports that potential candidates are carbon, hydrogen gas, carbon monoxide gas, metal zinc or metal copper.

The AgNO₃ Production unit receives silver from the Silver Recovery unit and the Ag₂SO₄ Reduction unit. Here silver is reacted with hot nitric acid to form silver nitrate. Silver nitrate is then recycled back to the Iodine Precipitation Tank and reused in precipitation of AgI and AgCl.

The solubility of silver and other selected compounds is listed in Appendix A. The main chemical reaction and side reaction equations of precipitation and silver recovery are summarized in Appendix B.

4.3 ION EXCHANGE

The Ion Exchange alternative would use a chloride-specific ion exchange resin that would have to be developed for this application. A PFD was not developed for the Ion Exchange option because the technology does not presently exist. The excess MOG scrub solution would undergo filtration before being passed through an ion exchange column containing this special resin. The chlorides - depleted column effluent would be sent to the LLW Evaporator Feed Tank (TK-400) to permit the recycle of other dissolved chemicals and radionuclides to the melter. Meanwhile, the ion exchange bed would undergo periodic elution with dilute caustic solution to recover the chlorides. The spent eluant stream would undergo sampling and analysis before being neutralized, possibly concentrated, and finally sent to solidification.

Another approach to chlorides purge by means of Ion Exchange would be to selectively remove dissolved radionuclides from the excess MOG scrub solution. The resulting ion exchange effluent stream would be successively concentrated, processed into grout, and purged from the plant. In addition to chlorides, this approach would also purge other chemical species such as fluorides, nitrates, phosphates and sulfates from the plant recycle loop. Because these other species are much more abundant than chlorides, the volume of the grout stream would increase by several fold relative to a chloride-specific design. Since such an increase in grout production was deemed unacceptable, this alternate approach to Ion Exchange was rejected.

5.0 DISCUSSION OF ALTERNATIVES

5.1 FUNCTIONS AND REQUIREMENTS

There are no specific functions or requirements documents which set the basis for a chloride purge system. The basis for this study is set by the TWRS Facility Configuration Study flowsheets and the modifications specified on Attachment 1 to this study. The following items are specific requirements based on the Reference Flowsheet and Attachment 1.

1. Receive the excess scrub solution purge from the Melter Offgas System. This aqueous stream contains radionuclide contaminants and cold chemical species originally volatilized from the melter, including chlorides and other halides. The mass flow rate and chemical breakdown of this stream are as follows:

Flow Rate, 8754 kg/hr

Volumetric Rate, 0.146 m³/min (38.6 gpm)

<u>Component</u>	<u>wt%</u>
H ₂ O	98.12
HNO ₃	0.50
HCl	0.17
HF	0.53
HI	5.19E-05
H ₃ PO ₄	0.31
H ₂ SO ₄	0.051
NaOH	0.32
KOH	4.66E-03

As specified by Attachment 1, the chloride content of this scrub solution purge stream reflects a 50 percent increase in the plant feed chlorides over the levels shown in the plant material balance.

2. To the extent possible, selectively separate the chlorides from the other constituents of the excess MOG scrub solution purge.
3. After selective removal of the chlorides, recycle the other constituents of the MOG scrub solution purge to the Feed Preparation System. In this way, these species will be returned to the melter and ultimately be incorporated into the product glass.
4. Decontaminate the chlorides purge to permit this stream to be processed through contact maintained equipment. Verify the effectiveness of this decontamination by sampling and analysis.

5. Process the chlorides purge into grout or a similar solid waste form. Place the grout in disposal containers before removal from the vitrification facility.
6. The plant process liquid waste that passes through the Process Condensate Recycle Tanks (TK-800A,B,C) must remain clean and free of dissolved halides.

5.2 ASSUMPTIONS, UNCERTAINTIES AND PROCESS CONCERNS

5.2.1 Distillation

The Distillation process design is very preliminary, and is intended for scoping purposes only. There are a number of process concerns that must be resolved before the final design configuration can be established. These concerns are listed below.

1. The process simulator used to model the Distillation Option for chloride removal was Aspen Plus. A significant area of concern for the Distillation Option is the accuracy of the equilibrium data used by Aspen for the ternary acid system (HCl, HNO_3 , HF). The literature data (Reid, et al.) for the binary system of HCl/ HNO_3 show that these two components can be easily separated by distillation, as predicted by the Aspen model. However, the literature data predict that the HCl is more volatile than predicted by the Aspen model, therefore the separation of these components can be achieved more readily. Of course, Aspen is accounting for the effects of other components in the system on overall volatility.
2. A more serious concern regarding the accuracy of the Aspen simulator came when the MOG scrub solution evaporator was modeled. Two Aspen data packages were tried in the evaporator simulation. The results for one of the packages showed all HF leaving in the evaporator overhead. The results of the second package showed a split of the HF between the overhead and bottoms. The calculated value for the HF equilibrium constant for one data package was nearly 100 times that of the other package.

Because of the uncertainty in the disposition of the HF in the evaporator, the conservative approach of adding a HF/HCl distillation column to the Distillation Option was taken. The HF/HCl distillation column is sized to process all of the HF in the feed, however the evaporator overhead stream is shown on the PFD as being returned to the LLW feed preparation area, assuming it has a significant fluoride content.

3. A related issue is the appropriate rejection of water from the incoming evaporator feed. The concentration of this stream by evaporation should promote the recombination of ionic H^+ and Cl^- to form molecular HCl, especially after

the addition of concentrated nitric acid. Because of its volatility, molecular HCl can be rejected to the overhead product of a distillation column, and thereby be purged from the process recycle loop.

A higher concentration factor across the evaporator would reduce the volume of the bottoms product sent to distillation. This would probably reduce the amount of nitric acid needed to achieve a given level of chloride rejection. This would be a significant benefit, since the neutralization of the contaminant-bearing bottoms from the HCl Stripping Column (T-06) is itself a major concern.

However, possible disadvantages that might limit any increase in evaporator boil off include:

- a) Increased fouling of the evaporator heat transfer surfaces will be incurred. There is an upper limit on the allowable concentration of dissolved solids in a boiling liquid, beyond which unacceptable scaling on the heated surfaces will occur. Forced circulation evaporators can achieve bottoms concentrations up to 500,000 ppm total dissolved solids (TDS) by suppressing vapor formation next to the heat transfer surfaces. However, these evaporators require a high capacity axial flow pump that must have periodic contact maintenance. Kettle type or natural circulation thermosyphon evaporators, which allow vapor formation against hot surfaces, are more susceptible to scaling. Consequently, they probably have a lower limit on acceptable TDS.
- b) A higher concentration factor across the evaporator will decrease the water content of the HCl Stripping Column bottoms. This might adversely affect the solubilities of the radionuclides and non-volatile inorganics that should remain dissolved to avoid excessive fouling of the Reboiler (EC-07).

4. Optimum Nitric Acid Addition

The presence of water and dissolved sodium and potassium in the Evaporator bottoms may suppress chloride volatility. The addition of concentrated nitric acid to this bottoms stream promotes the combination of ionic H^+ and Cl^- to form molecular HCl, which has a higher volatility. A sufficient volume of acid must be added to permit a reasonable, although not necessarily complete, overhead rejection of chloride by the HCl Stripping Column and the HCl Rectifying Column.

At the same time, however, the loss of concentrated nitric acid to the HCl Stripping Column bottoms should not create an excessive demand for neutralization chemicals, since these chemicals will be recycled to the melter. According to the current material balance, neutralization of the nitric acid in the bottoms stream would have one of the following consequences.

- (a) Essentially all of the calcium oxide (CaO) and lithium oxide (Li_2O) would have to be removed from the dry glass formers sent to the melter. The same amount of calcium and lithium would be added to the process in the form of calcium hydroxide ($\text{Ca}(\text{OH})_2$) and lithium hydroxide (LiOH) for neutralization of the nitric acid in the column bottoms. This approach would avoid any increase LLW glass production. However, it would also increase the volume of the LLW melter process slurry feeds. This could have an impact on the sizing of the melter, or of tanks in the Feed Preparation System. Also, the complete elimination of two constituents from the glass former mix may reduce the plants ability to optimize the waste oxide loading in the product glass under varying feed compositions.

or,

- (b) Neutralization of the nitric acid with sodium hydroxide would increase the total sodium entering the plant by 12.5 Mg/day. Assuming that the sodium content of product glass would remain at 18.5 wt%, the resulting increase in total life-of-plant glass production would be over 33 percent.

The avoidance of either of these consequences would require a reduction in nitric acid consumption. This might be accomplished by one or more of the following design changes:

- (i) Pump some of the acidic bottoms from the HCl Stripping Column back to a higher point on the column to re-use some of the nitric acid.
- (ii) Increase the rejection of excess water by the Evaporator (EV-01)
- (iii) Introduce a stripping agent such as live steam or air to the bottom of the HCl Stripping Column (T-06)

5. Behavior of Radionuclides

The Aspen computer model used for this study did not model the behavior of cesium, technetium and other radionuclides in the distillation column feed. Ideally, these species should be completely non-volatile and report to the column bottoms. If any of these species volatilize and enter the chlorides product stream, additional decontamination measures will be needed. This would probably involve running the chlorides product stream through an ion exchange column. Such a design change would, of course, add to the cost and complexity of the Chlorides Purge System.

6. Selection of Scrub Filter

It is assumed that for Scrub Filter (F-621 A&B), a non-precoated filter will provide adequate separation efficiency for solids from the MOG scrub solution. If a precoated filter is later determined to be necessary, additional equipment will be required for the diatomaceous earth used for filter coating. The equipment will include a tank with pump, agitator and other appurtenance.

7. Air In-Leakage to Distillation Train

It is assumed that the air in-leakage into the subatmospheric distillation system is at a rate of 80 SCFM. If the air in-leakage rate is later determined to be lower, a water ejector venturi may be considered for evacuating the in-leakage air instead of a blower. This in-leakage must be accounted for in re-sizing the Melter Offgas System.

8. Disposition of Vent from Distillation Train

It is assumed that the discharge from Blower (MB-17) will be tied into the quenched melter offgas streams entering the existing LLW Venturi Scrubbers (SC-615 A&B). The acid gases from the distillation system will be scrubbed out in the venturi scrubber.

9. Nitrate Recycle and NO_x Abatement

The impacts of nitrate recycle on the melter and on the NO_x abatement equipment will have to be investigated. The addition of nitric acid to volatilize the HCl increases the nitrate to the melter. According to Attachment 1, most of the nitrate will be converted in the melter to nitrogen gas with 6000 ppmv forming NO_x. Because of the increase in the offgas volume as a result of an increase in nitrogen, some increase in NO_x is expected. This increase in NO_x generation from the melter may increase the size of the existing NO_x abatement system.

5.2.2 Precipitation

1. Co-Precipitation of Radionuclides

The co-precipitation of radionuclides may occur together with the precipitation of AgCl. It may be difficult if not impossible to separate the radionuclide precipitates from the AgCl. Therefore the chloride waste form may have an unacceptable level of radioactivity for final disposal.

2. Co-Precipitation of Cold Chemicals

The co-precipitation of some cold chemical species together with AgCl will increase the volume of the final chloride waste form. As shown in the Appendix B, silver sulfate (Ag_2SO_4) and silver phosphate ($\text{Ag}_3(\text{PO}_4)_2$) co-precipitates with AgCl. These two species will follow the AgCl to the Ag Recovery unit where they will react with aluminum to form aluminum sulphate ($\text{Al}_2(\text{SO}_4)_3$) and aluminum phosphate (AlPO_4). The amount of sulfate in the MOG scrub solution is small compared to the chloride. However, there is a significant amount of phosphates and it will increase the volume of the final chloride waste form considerably.

3. Silver Recovery

The need for Silver Recovery units increases the complexity of the Precipitation option. Silver recovery is necessary to limit the amount of silver recycled to the melter and to eliminate silver from the chloride waste form. The recovery of silver will also reduce the life-cycle cost associated with the AgNO_3 reagent. The unit operations for Silver Recovery and Ag_2SO_4 Reduction are yet to be defined. The uncertainties associated with the recovery of silver from silver salts may require further investigation, and possibly, technology development.

4. Chlorides Recycle to Melter

It is assumed acceptable for some chlorides to be recycled to the melter. The solubility of AgCl is dependent on the temperature of the solution as well as the presence of other ionic species. It is assumed that most of the AgCl will be dissolved in the acidic solution with some AgCl remaining as precipitate with AgI. After the silver is recovered, this small amount of chloride is recycled back to the melter together with the iodide.

5. Processing of Silver Iodide Precipitate

The silver iodide precipitate is removed by filtration and is now shown as being recycled to the LLW Feed Preparation System. There is a significant risk, however, that a large fraction of this iodine recycle will simply re-volatilize in the melter. Most of it will then removed from the melter offgas by wet scrubbing, and eventually have to be re-precipitated as silver iodide. However, system operating cost and product quality considerations both favor minimizing the loss of silver to the LLW glass. Correcting this problem would require that the silver iodide recycle pass through a new silver recovery step. This, of course, would further increase the size and complexity of the Chlorides Purge System.

5.3 SUMMARY COMPARISON

5.3.1 Process Flowsheet/Facility Design Impacts

The process flowsheet impacts resulting from the adoption of the Distillation alternative are shown on the Distillation PFD (Attachment 2)

The Chloride Purge System receives the excess MOG scrub solution that was previously re-cycled to the Evaporate Feed Tank (TK-400) in the Case 4 design. The Chloride Purge System ties back into the base case LLW plant design with the following streams:

- (a) The contaminant-bearing distillation bottoms stream accumulated in the Recycle Neutralization Tank (TK-21) and periodically recycled to the LLW Feed Preparation System. This stream is first neutralized with calcium and lithium compounds directed from the mixed glass forms stream.
- (b) The excess water rejected as overhead condensate from the Evaporator (EV-23) before being sent to the existing Process Condensate Recycle Tanks (TK-800A,B,C).
- (c) The overhead condensate from Evaporator (EV-01) that, if contaminated with fluorides, must be recycled to the LLW Feed Preparation area for re-evaporation in the existing EV-402.
- (d) The noncondensable vent stream from the distillation columns that is recycled to the suction side of the existing LLW Venturi Scrubber (SC-615A,B) for reabsorption of acid gasses.

The Chloride Purge System also produces a new plant effluent stream in the form of grout filled drums containing immobilized chlorides.

The most significant impacts to Utility Systems resulting from the new Chlorides Purge System are:

- (a) An increase in total process heat demand resulting in the addition of a new Electric Process Steam Generator (EV-1124F) and appurtenances.
- (b) A corresponding increase in the total process cooling demand resulting in increases in the capacities of the process cooling water system and the cooling tower.

The facility design impacts (refer to Attachment 6) associated with the Distillation alternative consists of:

- (a) The addition of a new Grout Room measuring 16.4 meters by 17.4 meters near the northeast corner of the Separations/LLW Vitrification Building. This room is sized to contain the grout mixing operations and sufficient drum storage space to allow 21 days of grout curing.
- (b) The positioning of some of the new Chloride Purge System equipment items in floor space previously occupied by the Melter Cut-Up Cell, resulting in an extension of the cell length from 15.2 m (50'-0") to 21.9 m (72'-0"). The combined width of the Chloride Purge Area and Melter Cut-Up Cell remains unchanged at 22.9 m (75'-0").

Detailed flow sheets and facility layouts were not developed for the Precipitation and Ion Exchange option.

5.3.2 Operability/Complexity

- The Distillation alternative requires continuous and reliable control of several operating parameters, such as compositions, temperatures, pressures and flow rates. It also requires the addition of several pieces of rotating equipment to the hot cell. Distillation should be less complex than Chlorides Precipitation, but is still more complex than would be desired. However, if no better technique can be found, the Distillation alternative should have acceptable complexity and operability.
- The Chlorides Precipitation alternative is a highly complex process with significant technical uncertainties. Because of this, it is not a viable candidate for this application.
- If a chloride-specific ion exchange resin could be developed, it may significantly simplify the design and operation of a selective chlorides purge system. This option would require further investigation.

5.3.3 Maintainability

- The use of remotely operable process connectors should make each equipment item provided by the Distillation alternative independently removable for maintenance. The use of these connectors also requires the associated process equipment to be operated at a slight negative gauge pressure to prevent outleakage to the process cell.

If process considerations were to dictate operation of the distillation columns at a positive gauge pressure, the remotely operable connectors would have to be replaced by leak tight, contact maintained connectors. This would preclude the selective removal of individual

equipment items for maintenance. As a result, the distillation columns and their appurtenant equipment might have to be built as a module that would be removable from the process cell only as a complete unit. Such a change would reduce the maintainability of the affected items.

- The Precipitation System will be remotely maintainable. The number of tanks, pumps and operating units for the Precipitation option is higher than that for the Distillation and Ion Exchange options, and therefore will require more maintenance.

5.3.4 Maturity of Technology

- The technology to remotely perform the unit operations required by the Distillation alternative appears to be mature and readily available. However, the ability of computer-based modelling techniques to accurately predict the behavior of each chemical specie, as well as the overall system performance, is an area of uncertainty. For this reason, laboratory or pilot scale testing over the entire range of system feed compositions and operating conditions will probably be needed. Such a test program could also define the optimum rejection of excess water upstream of the distillation columns, and the appropriate concentration of nitric acid in the column feed.
- The technology to precipitate chlorides as silver chlorides is readily available. The technology to recover silver from silver salts (AgCl , AgI , AgF , AgNO_3 , Ag_2SO_4) may require some development.
- At the present time, there is no commercially available ion exchange resin that will selectively remove chloride ions from an aqueous solution. However, representatives of Eichrom Industries in Darien, Illinois, maintain the realistic possibility of developing such a resin.

Eichrom reports that a fluoride specific regenerable resin is now under development, and should soon be ready for commercial testing. This absorbent is a specially designed organic molecule known as a cryptand. The molecule is made up of three linear strands joined together at each end to form a three-dimensional structure resembling a hollow football. The individual strands are selected to form an internal cage structure having a predetermined size. This gives the cryptand a high degree of selectivity in capturing only ions of a compatible physical size. Ion absorption is typically performed under acidic conditions. The subsequent resin regeneration makes use of an alkaline eluant which causes the cryptand molecule to expand and release the ions trapped inside. Resin make-up requirements are conservatively estimated to be 10 to 20 percent of the total inventory per year.

A chloride specific cryptand would be similar to the fluoride-specific molecule now being developed. However, the size of its internal cage structure would have to be increased, since chloride is a larger ion than fluoride. There is some possibility that this increase in molecular pore size could decrease chloride selectivity due to interactions with other ions of comparable size. The extent of this interaction would depend on the actual composition of the solution being treated.

Eichrom estimates that the cost of developing a chloride-specific resin would be about \$200,000-250,000. The duration of the development program is estimated to be 2-2½ years.

5.3.5 Schedule Impacts

- As noted above, the adoption of the Distillation alternative would require the generation of confirmatory design data by a laboratory or pilot scale test program covering the entire range of system feed compositions and operating conditions. This test program should be completed early enough to permit the use of the test results no later than the detailed phase of plant design.
- Because the precipitation alternative is deemed to be technically unsuitable, no assessment is made of its potential schedule impacts.
- A program to develop the chloride-specific resin needed by the Ion Exchange alternative would require 2-2½ years. It would be necessary to determine the feasibility of resin development as soon as possible to permit, if necessary, the adoption of an alternate course of action without delaying the overall plant schedule.

5.3.6 Regulatory Impacts

Regulatory Impacts does not appear to be a discriminating issue between the alternatives.

5.3.7 Safety

All three chlorides purge processes should be compatible with a safe plant design.

5.3.8 Cost

- The basis for the differential TEC for a facility incorporating chloride purge equipment (relative to Case 4C) is shown on Attachment 7. The TEC for the chloride purge distillation and grouting equipment is \$48,350,000. The high

equipment cost is driven by the required metallurgy (Hastelloy and Inconel). The differential cost for the facility which houses the chloride purge system is \$8,660,000. The total differential TEC for the chloride purge and grouting system is \$57,010,000. The operating cost of the chloride purge system is \$8,260,000/yr, as shown on Attachment 4. This operating cost is exclusive of labor.

- The capital cost for the Precipitation option has not been developed. However, the operating cost of the Precipitation option would be prohibitively high (\$480 million of AgNO_3) if the silver were disposed with the chloride waste form as AgCl . The cost will be reduced with recovery and reuse of the silver. However, the capital and life-cycle cost of silver recovery may cause this option to become more expensive than the Distillation and the Ion Exchange options.

APPENDIX A

SOLUBILITIES OF SELECTED COMPOUNDS

References: Kirk-Othmer "Encyclopedia of Chemical Technology," 3rd Edition.
 Perry's Chemical Engineers' Handbook. 6th Edition. McGraw-Hill.
 Lange's Handbook of Chemistry. 12th Edition. McGraw-Hill.

Ref.	MW	Compound	Solubility	Reference Temp, °C
Kirk-Othmer	311.7936	Ag ₂ SO ₄	7.96	g/L H ₂ O 20
Kirk-Othmer	143.321	AgCl	0.0019	g/L H ₂ O 25
Kirk-Othmer	126.8664	AgF	1800	g/L H ₂ O 25
Kirk-Othmer	234.7725	AgI	0.0000026	g/L H ₂ O 25
Kirk-Othmer	169.8729	AgNO ₃	2220	g/L H ₂ O 20
Kirk-Othmer	275.77	Ag ₂ CO ₃	0.5	g/L H ₂ O 100
Lange's	418.62	Ag ₃ PO ₄	0.06	g/L H ₂ O not available
Kirk-Othmer	110.986	CaCl ₂	745	g/L H ₂ O 20
Perry's	78.0768	CaF ₂	0.146	g/L H ₂ O 25
Perry's	162.094	Ca(HCO ₃) ₂	166	g/L H ₂ O 20
Kirk-Othmer	293.889	CaI ₂	676	g/L H ₂ O room temp.
Kirk-Othmer	136.1376	CaSO ₄	2.09	g/L H ₂ O 30
Lange's	310.18	Ca ₃ (PO ₄) ₂	0.3	g/L H ₂ O 25
Perry's	278.106	PbCl ₂	9.9	g/L H ₂ O 20
Lange's	255.1982	PbCO ₃	0.0011	g/L H ₂ O 20
Perry's	245.1968	PbF ₂	0.64	g/L H ₂ O 20
Kirk-Othmer	461.009	PbI ₂	0.44	g/L H ₂ O 20
Perry's	303.2576	PbSO ₄	0.056	g/L H ₂ O 40
Kirk-Othmer	303.2576	PbSO ₄	0.0425	g/L H ₂ O 25
Lange's	811.59	Pb ₃ (PO ₄) ₂	insoluble	
Lange's	168.36	CsCl	1870	g/L H ₂ O 20
Lange's	151.9	CsF	3220	g/L H ₂ O 18

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Ref.	MW	Compound	Solubility	Reference Temp, °C
Lange's	259.81	CsI	765	g/L H ₂ O 20
Lange's	361.87	Cs ₂ SO ₄	1790	g/L H ₂ O 20
Lange's	194.91	CsNO ₃	230	g/L H ₂ O 20
Lange's	325.82	Cs ₂ CO ₃	very soluble	
Lange's	147.64	SrCO ₃	0.01	g/L H ₂ O 25
Lange's	158.52	SrCl ₂	529	g/L H ₂ O 20
Lange's	125.63	SrF ₂	0.11	g/L H ₂ O 20
Lange's	341.42	SrI ₂	1780	g/L H ₂ O 20
Lange's	452.85	Sr ₃ (PO ₄) ₂	insoluble	
Lange's	183.7	SrSO ₄	0.13	g/L H ₂ O 20

APPENDIX B

SUMMARY OF CHEMICAL REACTIONS

(1) IODIDE PRECIPITATION

TARGET REACTION: $\text{HI(aq)} + \text{AgNO}_3\text{(aq)} = \text{AgI(s)} + \text{HNO}_3\text{(aq)}$

OTHER REACTIONS:

(2) CHLORIDE PRECIPITATION

TARGET REACTION: $\text{AgCl(aq)} = \text{AgCl(s)}$

OTHER REACTIONS:

(3) FLUORIDE PRECIPITATION

REACTION: $2\text{AgF(aq)} + \text{Ca(OH)}_2 = \text{CaF}_2\text{(s)} + 2\text{Ag}^+\text{(aq)} + 2\text{OH}^-\text{(aq)}$

(4) Ag RECOVERY FROM AgCl

REACTION: $3\text{AgCl(aq)} + \text{Al(s)} = \text{AlCl}_3\text{(aq)} + 3\text{Ag(s)}$

(5) Ag RECOVERY FROM EXCESS AgNO₃

SILVER SULFATE PRECIPITATION:

REACTION:

$\text{Ag}_2\text{SO}_4\text{(s)} + \text{REDUCING AGENT} = 2\text{Ag(s)} + \text{SO}_2\text{(g)} + \text{CO}_2\text{(g)}$ (OR $\text{H}_2\text{O(l)}$)

REDUCING AGENT = C, H₂, CO

OR MAIN REACTION

REDUCING AGENT, M = Zn OR Cu

"=" denotes equilibrium reaction

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ATTACHMENT 1

**COMBINATION MELTER
VOLATILITY ASSUMPTIONS**

VOLATILITY ASSUMPTIONS FOR FLUOR DANIEL MELTER OFFGAS STUDY

Author: A. L. Boldt

Date: January 31, 1995

Per your request, the assumptions to be used for the preliminary evaluation of LLW melter offgas processes is presented below. These assumptions were developed by consultation with B. A. Higley.

The feed to the LLW melter should adjust the chloride inventory up be a factor of 1.5. (DSI, L. W. Shelton to B. A. Higley, "Estimated Chloride Inventory of Hanford Tank Waste," dated August 30, 1994).

Component Volatility	
Component	% Volatile
B2O3	25 % as NaBO2
C	100 % as CO2 (organic and inorganic carbon)
CdO	33 %
Cl-	95 %
Cs2O3	33 %
F-	67 %
I-	100 %
K2O	Keep K/Na ratio equal to melter feed K/Na ratio
MoO3	5 %
Na2O	1 %
PbO2	33 %
Ru2O3	33 %
Se2O3	33 %
Tc2O7	50 %
TeO3	33 %
SO4	90 % as SO2 10 % as SO3
P2O4	20 %
NOx	6,000 ppm on a noncondensable basis

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ATTACHMENT 2

**DISTILLATION ALTERNATIVE PFD
AND
MATERIAL BALANCE**

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DEPARTMENT OF ENERGY
HANFORD WASTE VITRIFICATION PROJECT
CONTRACT NO. 04436303 CWBS 2018
DATE: 03/28/95
BY: H. SNG CHK'D: S.D. SHARP

Chlorides Purge by Distillation (For Low-Level Waste Melters at 200 Megagrams per Day.													
Stream No.	1	2	3	4	5	6	7	8	9	10	11	12	13
kg/hr													
H ₂ O	8,589	7,730	859	112	971	742	229	129	100	1300	161	102	59
HNO ₃	43.4	0	43.4	1,386	1,429	1,429	3.63e-01	3.63e-01	9.01e-05	1,860	4.90e-01	0	4.90e-01
HCl	14.7	0	14.7	0	14.7	1.02e-01	14.6	13.5	1.06	1.76	0	0	0
HF	46.8	0	46.8	0	46.8	1.60e-04	46.8	11.2	35.6	69.4	0	0	0
HI	4.54e-03	0	4.54e-03	0	4.54e-03	4.54e-03	0	0	0	5.21e-03	0	0	0
H ₃ PO ₄	26.8	0	26.8	0	26.8	26.8	0	0	0	42	0	0	0
H ₂ SO ₄	4.50	0	4.50	0	4.50	4.50	0	0	0	6.24	0	0	0
NaOH	28.0	0	28.0	0	28.0	28.0	0	0	0	28	0	0	0
KOH	4.08e-01	0	4.08e-01	0	4.08e-01	4.08e-01	0	0	0	4.08e-01	0	0	0
NaCl											21.7		21.7
CaF ₂											21.8		21.8
FLOW, kg/hr	8,754	7,730	1,024	1,498	2,521	2,231	291	154	137	3,308	205	102	103

Attachment 2-3

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DEPARTMENT OF ENERGY
HANFORD WASTE VITRIFICATION PROJECT
CONTRACT NO. 04436303 CWBS 2018
DATE: 03/28/95
BY: H. SNG CHK'D: S.D. SHARP

Chlorides Purge by Distillation (For Low-Level Waste Melters at 200 Megagrams per Day.													
Stream No.	1	2	3	4	5	6	7	8	9	10	11	12	13
WT %													
H ₂ O	98.12	100	83.89	7.48	38.52	33.26	78.69	83.77	72.99	39.30	78.54	100	57.38
HNO ₃	0.50	0	4.24	92.52	56.68	64.05	0.12	0.24	6.58e-05	56.23	0.24	0	4.80e-01
HCl	0.17	0	1.44	0	0.58	4.59e-03	5.02	8.77	0.77	0.05	0	0	0
HF	0.53	0	4.57	0	1.86	7.17e-06	16.08	7.27	25.99	2.10	0	0	0
HI	5.19e-05	0	4.43e-04	0	1.80e-04	2.04e-04	0	0	0	1.58e-04	0	0	0
H ₃ PO ₄	0.31	0	2.62	0	1.06	1.20	0	0	0	1.28	0	0	0
H ₂ SO ₄	0.05	0	0.44	0	0.18	0.20	0	0	0	0.19	0	0	0
NaOH	0.32	0	2.73	0	1.11	1.25	0	0	0	0.85	0	0	0
KOH	4.66e-0	0	4.00e-02	0	2.00e-02	1.83e-02	0	0	0	1.00e-02	0	0	0
NaCl											10.59		21.07
CaF ₂											10.63		21.17

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Attachment 2-4

- Notes: (1) Some HF may be volatilized to the evaporator overhead. For conservatism, all the HF is assumed to enter the evaporator bottoms (Stream No. 3).
(2) All phosphoric acid, sulfuric acid, sodium hydroxide and potassium hydroxide are assumed to remain in the distillation bottoms (Stream No. 6).
(3) Further separation of HF from HCl (Stream No. 8) may be achieved by optimizing the HF stripper column.
(4) For Stream No. 10, assume complete reaction of calcium hydroxide with acidic species with no competitive reactions from sodium hydroxide and potassium hydroxide.
(5) For stream No. 11, assume stoichiometric reaction of calcium hydroxide with hydrofluoric acid with no competitive reactions from hydrochloric acid and nitric acid.
(6) Stream No. 13 is based on a 5 M sodium ion concentration.

Figure 2-1. Process Flow Diagram
Offgas Development Chlorides Purge
By Distillation.

Attachment 2-5/6

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ATTACHMENT 3

**DISTILLATION ALTERNATIVE
EQUIPMENT LIST**

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EQUIPMENT LIST
FOR CHLORIDES PURGE BY DISTILLATION (FOR LLW MELTER)

TYPE CHANGE	EQUIPMENT DESCRIPTION	EQUIP. I.D.	CAPACITY/ FLOWRATE	PHYSICAL SIZE (DIA X H)	MATERIAL	COMMENTS
	EVAPORATOR	EV-01	6.24 MW	7.32 m L X 3.66 m W X 9.45 m H	HASTELLOY C-276	SIMILAR TO EV-402
	CONDENSER	EC-02	6.36 MW	PART OF EV-01	HASTELLOY C-276	SIMILAR TO EC-403
	DISTILLATION FEED TANK	TK-03	14.4 m ³	2.74 m ID X 2.44 m T/T	ALLOY 20	SIMILAR TO TK-611 WITH DIFFERENT METALLURGY
	PUMP	P-04	22.7 m ³ /hr, 200 kPa	MOUNTED ON TK-03	ALLOY 20	HWVP TRANSFER PUMP WITH DIFFERENT METALLURGY
	PREHEATER	EC-05	76 kW	0.30 m ID X 1.22 m L	ALLOY 20	NEW EQUIPMENT
	HCl STRIPPING COLUMN	T-06		0.46 m ID X 8.08 m T/T	ALLOY 20	NEW EQUIPMENT
	HCl REBOILER	EC-07	938 kW	0.61 m ID X 3.05 m L	ALLOY 20	NEW EQUIPMENT
	HCl DISTILLATION TANK	TK-08	8.7 m ³	2.74 m ID X 1.52 m T/T	ALLOY 20	NEW EQUIPMENT
	PUMP	P-09	22.7 m ³ /hr, 131 kPa	MOUNTED ON TK-08	ALLOY 20	HWVP TRANSFER PUMP WITH DIFFERENT METALLURGY
	HCl RECTIFYING COLUMN	T-10		0.46 m ID X 5.94 m T/T	HASTELLOY C-276	MOUNTED ON TK-08
	HCl CONDENSER	EC-11	645 kW	0.61 m ID X 2.44 m L	HASTELLOY C-276	SIMILAR TO EC-403
	HCl OVERHEAD ACCUMULATOR	TK-12	0.62 m ³	0.61 m ID X 2.13 m T/T	HASTELLOY C-276	NEW EQUIPMENT
	HF STRIPPING COLUMN	T-13		0.30 m ID X 7.01 m T/T	HASTELLOY C-276	NEW EQUIPMENT
	HF REBOILER	EC-14	205 kW	0.46 m ID X 1.83 m L	HASTELLOY C-276	NEW EQUIPMENT
	HF CONDENSER	EC-15	322 kW	0.46 m ID X 2.13 m L	HASTELLOY C-276	SIMILAR TO EC-403
	HF OVERHEAD ACCUMULATOR	TK-16	0.25 m ³	0.46 m ID X 1.52 m T/T	HASTELLOY C-276	NEW EQUIPMENT
	BLOWER	MB-17	129 Nm ³ /hr, 3.73 kW	1.22 m X 0.91 m	HASTELLOY C-276	SIMILAR TO BLOWER MB-700A&B
	CHLORIDES PURGE NEUTRALIZATION TANK	TK-18A&B	14.4 m ³	2.74 m ID X 2.44 m T/T	HASTELLOY C-276	SAME AS TK-611
	PUMP	P-19A&B	22.7 m ³ /hr, 76 kPa	MOUNTED ON TK-18A&B	HASTELLOY C-276	HWVP TRANSFER PUMP

TYPE CHANGE: M = MODIFICATION, A = ADDITION, D = DELETION
ITEMS MARKED WITH "D" WILL NOT APPEAR ON NEXT REVISION

EQUIPMENT LIST
FOR CHLORIDES PURGE BY DISTILLATION (FOR LLW MELTER)

TYPE CHANGE	EQUIPMENT DESCRIPTION	EQUIP. I.D.	CAPACITY/ FLOWRATE	PHYSICAL SIZE (DIA X H)	MATERIAL	COMMENTS
	SAMPLE PUMP	P-20A&B	11.4 m ³ /hr, 497 kPa	MOUNTED ON TK-18A&B	HASTELLOY C-276	HWVP SAMPLE PUMP
	RECYCLE NEUTRALIZATION TANK	TK-21	14.4 m ³	2.74 m ID X 2.44 m T/T	316L SS	SAME AS TK-611
	PUMP	P-22	22.7 m ³ /hr, 159 kPa	MOUNTED ON TK-21	316L SS	HWVP TRANSFER PUMP
A	EVAPORATOR	EV-23	97 kW	0.91 m L X 0.61 m W X 2.74 m H	316L SS	FORCED-CIRCULATION EVAPORATOR.
A	PUMP	P-24	22.7 m ³ /hr, 103 kPa	INCLUDED WITH EV-23	316L SS	
A	CONDENSER	EC-25	93 kW	0.30 m ID X 1.52 m L	316L SS	SIMILAR TO EC-1101-4.
A	GROUT FEED TANK	TK-27	2.6 m ³	1.52 m ID X 1.52 m T/T	316L SS	SIMILAR TO TK-1200-3B.
A	GROUT FEED PUMP	P-28A&B	4.3 m ³ /hr, 97 kPa		316L SS	SIMILAR TO P-1160-3B.
A	CALCIUM HYDROXIDE FEED TANK	TK-29	1.9 m ³	1.37 m ID X 1.52 m T/T	316L SS	SAME AS TK-1200-3B.
A	CALCIUM HYDROXIDE FEED PUMP	P-30	1.6 m ³ /hr, 76 kPa		316L SS	SIMILAR TO P-1160-3B.
A	CALCIUM HYDROXIDE STORAGE TANK	TK-31	16 m ³	2.74 m ID X 2.74 m T/T	316L SS	SIMILAR TO TK-1014.
A	CALCIUM HYDROXIDE TRANSFER PUMP	P-32	3.2 m ³ /hr, 207 kPa		316L SS	SIMILAR TO P-1017.

Attachment 3-4

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EQUIPMENT LIST
FOR CHLORIDES PURGE BY DISTILLATION (FOR LLW MELTER)
EQUIPMENT IMPACTS TO EXISTING UTILITY SYSTEM

TYPE CHANGE	EQUIPMENT DESCRIPTION	EQUIP. I.D.	CAPACITY/ FLOWRATE	PHYSICAL SIZE (DIA X H)	MATERIAL	COMMENTS
A	PROCESS STEAM CONDENSATE/CONDENSER	EC-1102	26.4 GJ/hr		304L SS	MODIFICATION OF EXISTING EQUIPMENT EC-1102-4.
A	PROCESS COOLING WATER COOLER	EC-1103A	211 GJ/hr		304L SS PLATES	MODIFICATION OF EXISTING EQUIPMENT EC-1103A-4.
A	PROCESS COOLING WATER COOLER	EC-1103B	211 GJ/hr		304L SS PLATES	MODIFICATION OF EXISTING EQUIPMENT EC-1103B-4.
A	ELECTRIC PROCESS STEAM GENERATOR	EV-1124F	7.76 MW	THREE SECTIONS: 11.3 m X 6.10 m; 11.4 m X 1.83 m; AND 6.10 m X 2.44 m	CARBON STEEL	EQUIPMENT ADDED. SAME AS EV-1124A-4.
A	STANDBY ELECTRIC HEATER	EV-1125F	40.0 kW	INCLUDED WITH EV-1124F	N/A	EQUIPMENT ADDED. SAME AS EV-1125A-4.
A	PROCESS STEAM GENERATOR CIRCULATING PUMP	P-1127L	681 m ³ /hr, 69 kPa	INCLUDED WITH EV-1124F	304L SS	EQUIPMENT ADDED. SAME AS P-1127A-4.
A	PROCESS STEAM GENERATOR CIRCULATING PUMP	P-1127M	681 m ³ /hr, 69 kPa	INCLUDED WITH EV-1124F	304L SS	EQUIPMENT ADDED. SAME AS P-1127A-4.
A	BOILER FEED WATER CHEMICAL INJECTION PUMP	P-1128F	0.23 m ³ /hr, 1366 kPa	INCLUDED WITH EV-1124F	304L SS	EQUIPMENT ADDED. SAME AS P-1128A-4.
A	BLOWDOWN DRUM	TK-1129F	1.5 m ³	INCLUDED WITH EV-1124F	304L SS	EQUIPMENT ADDED. SAME AS TK-1129A-4.
A	CHEMICAL ADDITION TANK	TK-1130F	0.95 m ³	INCLUDED WITH EV-1124F	304L SS	EQUIPMENT ADDED. SAME AS TK-1130A-4.
A	PROCESS CONDENSATE PUMP	P-1137L	13.6 m ³ /hr, 1379 kPa		304L SS	EQUIPMENT ADDED. SAME AS P-1137A-4.
A	PROCESS CONDENSATE PUMP	P-1137M	13.6 m ³ /hr, 1379 kPa		304L SS	EQUIPMENT ADDED. SAME AS P-1137A-4.
A	PROCESS COOLING WATER PUMP	P-1138A	3179 m ³ /hr, 487 kPa		304L SS	MODIFICATION OF EXISTING EQUIPMENT P-1138A-4.

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EQUIPMENT LIST
FOR CHLORIDES PURGE BY DISTILLATION (FOR LLW MELTER)
EQUIPMENT IMPACTS TO EXISTING UTILITY SYSTEM

TYPE CHANGE	EQUIPMENT DESCRIPTION	EQUIP. I.D.	CAPACITY/ FLOWRATE	PHYSICAL SIZE (DIA X H)	MATERIAL	COMMENTS
A	PROCESS COOLING WATER PUMP	P-1138B	3179 m ³ /hr, 487 kPa		304L SS	MODIFICATION OF EXISTING EQUIPMENT P-1138B-4.
A	PROCESS COOLING WATER EXPANSION TANK	TK-1192	9.7 m ³	1.83 m ID X 3.66 m T/T	304L SS	MODIFICATION OF EXISTING EQUIPMENT TK-1192-4.
A	COOLING TOWER	CT-1561	378 GJ/hr			MODIFICATION OF EXISTING EQUIPMENT CT-1561-4.
A	TOWER WATER PUMP	P-1562A	5450 m ³ /hr, 600 kPa		CARBON STEEL	MODIFICATION OF EXISTING EQUIPMENT P-1562A-4.
A	TOWER WATER PUMP	P-1562B	5450 m ³ /hr, 600 kPa		CARBON STEEL	MODIFICATION OF EXISTING EQUIPMENT P-1562B-4.
A	TOWER WATER PUMP	P-1562C	5450 m ³ /hr, 600 kPa		CARBON STEEL	MODIFICATION OF EXISTING EQUIPMENT P-1562C-4.

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ATTACHMENT 4

DISTILLATION ALTERNATIVE
UTILITY SUMMARY

ANNUAL CONSUMABLES
FOR CHLORIDES PURGE BY DISTILLATION (FOR LLW MELTER)

UTILITY/ CHEMICAL DESCRIPTION	UNIT COST (\$/each)	QUANTIT Y (units/year)	COST (\$MM/year)
Raw Water ¹ (m ³ /yr)	3	162,800	0.49
Electricity ² (MWh/yr)	30	74,400	2.23
50/50 cement and flyash mixture (Mg/yr)	72 ³	996	0.07
92.5 wt% Nitric Acid (Mg/yr)	372 ⁴	13,120	4.88
50 wt% Sodium Hydroxide (Mg/yr)	250 ⁵	265	0.07
Calcium Hydroxide (Mg/yr)	62.3 ⁶	8,420	0.52
Annual Total ⁷			8.26

¹ Additional cooling tower makeup requirement.

² Include chloride removal system purge and additional power requirements for associated utility systems.

³ Unit price of 50/50 cement and flyash mixture is based on "Means Concrete Cost Data. 1993" 11th Annual Edition. The cost of flyash is assumed to be 70 percent of the cost of cement.

⁴ Unit price is based on "Chemical Marketing Reporter". January 13, 1995.

⁵ Unit price of sodium hydroxide is based on "CPI Purchasing", July, 1994. p. 42.

⁶ Unit price is based on "Chemical Marketing Reporter". January 13, 1995.

⁷ The increase in utility steam, compressed air, sanitary water and decon solution usage is assumed to be negligible.

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ATTACHMENT 5

**PRECIPITATION ALTERNATIVE
PFD**

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Figure 5-1. Process Flow Diagram
Offgas Development Chlorides
Purge by Precipitation.

Attachment 5-3/4

REV NO	DATE	REVISION DESCRIPTION	APPROVALS
001	2018PFD2	001	2B1BMACD212.CISS
ENGINEERING RELEASE		U.S. DEPARTMENT OF ENERGY	
REV _____ DATE _____		Richland Plant Office	
ERO		IC - ACIS-BALANCE	
REVISION	DATE	BY	
001		FLUOR DANIEL, INC.	
PROJECT NO.		ADVANCED TECHNOLOGY DIVISION	
STATION NO.		PROCESS FLOW DIAGRAM	
CHECKING NO.		OFFGAS DEVELOPMENT	
APPROVER		CHLORIDES PURGE BY	
JOB NO.		PRECIPITATION	
CHECKED		HAWKINS WASTE VITRIFICATION PLANT	
DESIGNED		PLAN NUMBER 18	
DRAWN		DATE 18	
SCALE		REV NO	
2-18-18		2018	
NONE		1	
NONE		1	
NONE		0	
NEXT USED ON		ES-OP18-02	

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ATTACHMENT 6

**DISTILLATION ALTERNATIVE
FACILITY LAYOUT DRAWINGS**

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Figure 6-1. Separations/LLW Vitrification Building.

DETACHED PLAN "Y"
EL.-3.05M (-10'-0")

Attachment 6-3/4

CASE 4C OPTIMIZATION WITH CHLORIDES PURGE BY DISTILLATION

REV. NO.	DATE	REVISION DESCRIPTION	APPROVAL, SIGNATURE
001	ALT4CWOA	2838M-ACD210.C2-SS	
ENGINEERING RELEASE	REV. DATE	U.S. DEPARTMENT OF ENERGY	
END		Richland Field Office	
PROJECT NO.		FLUOR DANIEL, INC.	
PROJECT NAME		ADVANCED TECHNOLOGY DIVISION	
PROJECT DATE		PLAN EL. (AS NOTED)	
ENGINEERING NO.		SEPARATIONS/LLW	
ENGINEERING DATE		VITRIFICATION BUILDING	
APPROVED		TANK WASTE REMEDIATION SYSTEM	
DESIGNED		456303	
CHECKED		2018	
DATE	3-16-85	1/16" = 1'-0"	
BY	M. SCHULBERG	ES-ALT4W-01	
CLASSIFICATION	NONE	NOT NEEDED	1 A

Attachment 6-5/6

CASE 4C OPTIMIZATION WITH CHLORIDES PURGE BY DISTILLATION

REF NO.	DATE	PERSON SEARCHED	APPROVAL, TITLE		
CHRG.	ALT4CW1B	DISCARD	28BWJACD2:10.C2:SS		
ENGINEERING RELEASE		U.S. DEPARTMENT OF ENERGY National Field Office			
REV	DATE				
ENO					
ISSUING	DATE				
FILED IN		FLUOR DANIEL, INC. ADVANCED TECHNOLOGY DIVISION PLAN EL. 9.75M (32'-0") SEPARATIONS/LLW VITRIFICATION BUILDING			
SALES					
ENGINEERING SERVICE UNIT					
PROJECT UNIT					
ISSUING UNIT					
DISSEMINATION UNIT					
SALES/ISSUING		PROJECT TITLE TANK WASTE REMEDIATION SYSTEM PROJECT NUMBER 436303 ISSUE NO. 2018 FILED NO. 1/16-85			
SALES/ISSUING					
CHARGE					
NAME					
U.S. CHOLBERG	3-16-85				
CLASSIFIED					
NO	NOT NEEDED	ES-ALT4W-01	2	1	1

WHC-SD-WM-TI-702
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Figure 6-3. Section A-
Separations/LLW Vitrification
Building.

Attachment 6-7/8

CASE 4C OPTIMIZATION
WITH CHLORIDES PURGE
BY DISTILLATION

ON (A)
SHTS 1 & 2

REV. NO.	DESCRIPTION
1	ISSUED FOR CONSTRUCTION
2	REVISED TO REFLECT CHANGES
3	REVISED TO REFLECT CHANGES
4	REVISED TO REFLECT CHANGES
5	REVISED TO REFLECT CHANGES
6	REVISED TO REFLECT CHANGES
7	REVISED TO REFLECT CHANGES
8	REVISED TO REFLECT CHANGES
9	REVISED TO REFLECT CHANGES
10	REVISED TO REFLECT CHANGES

REV. NO.	DATE	DESCRIPTION	APPROVAL
1	11/18/85	ISSUED FOR CONSTRUCTION	W. J. SCHULBERG
ENGINEERING RELEASE		U.S. DEPARTMENT OF ENERGY	
REV. DATE		2818M/ACD2:10.C2:SS	
END		Richard Field Office	
DESIGNED BY		FLUOR DANIEL, INC.	
CHECKED BY		ADVANCED TECHNOLOGY DIVISION	
DRAWN BY		SECTION A	
REVISIONS		SEPARATIONS/LLW	
REVISIONS		VITRIFICATION BUILDING	
REVISIONS		TANK WASTE REMEDIATION SYSTEM	
REVISIONS		438303	
REVISIONS		2018	
REVISIONS		1/18" = 1'-0"	
REVISIONS		ES-ALT4W-01	
REVISIONS		3	
REVISIONS		A	

4/2/84

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Figure 6-4. Section B-
Separations/LLW Vitrification Building.

Attachment 6-9/10

-74'-0")

SECTION

B

SHT 1 & 2

CASE 4C OPTIMIZATION WITH CHLORIDES PURGE BY DISTILLATION

DATE REC.	ISSUING OFFICE
REFERENCE DRAWINGS	
NEXT USED ON	

REF ID	DATE	REVERSE DESCRIPTION	ATTENDING DETAILS	
COPIES	ALT4WCWOD	DISCARD	2B:18M:ACD2:10.C2:SS	
ENGINEERING RELEASE		U.S. DEPARTMENT OF ENERGY National Field Office		
KEY _____ DATE _____				
ERO _____				
FBI _____				
FIELD NO.	DATE	FLUOR DANIEL, INC. ADVANCED TECHNOLOGY DIVISION SECTION B SEPARATIONS/LLW VITRIFICATION BUILDING		
LA LAB				
ANALYST/INSTR. USE				
PROJECT NO.				
SYSTEM NO.		SECTION B SEPARATIONS/LLW VITRIFICATION BUILDING		
DISCLOSURE NO.				
SUPPLIER				
WASTE CRACKER				
CHARGE		WASTE REMEDIATION SYSTEM PROJECT NO. 436303 DATE 2018		
BY	3-16-95	SCALE 1/16" = 1'-0"	PROJECT NO.	
NAME	MSCHJOLBERG	DATE	REV	
LOCATION	IN	REVISION	4	4
NOTE	NOT RECD	ES-ALT4W-01	4	A

ATTACHMENT 7

CHLORIDES PURGE BY DISTILLATION FOR LOW-LEVEL WASTE MELTER
TEC COST ANALYSIS (X \$1,000)

Distillation Option TEC Analysis (x \$1,000)				
Description	DFC	ENG/PM/CM	Contingency	TEC
Vitrification Building Impact	\$ 3,749	\$ 2,437	\$ 2,474	\$ 8,660
Equipment	\$ 20,931	\$ 13,605	\$ 13,814	\$ 48,350
TOTAL	\$ 24,680	\$ 16,042	\$ 16,288	\$ 57,010