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TECHNOLOGY DEVELOPMENT IN SUPPORT OF THE TWRS
PROCESS FLOWSHEET

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7. Abstract

The Tank Waste Remediation System is to treat and dispose of Hanford's Single-Shell and Double-Shell Tank waste. The TWRS Process Flowsheet (WHC-SD-WM-TI-613 Rev. 1) described a flowsheet based on a large number of assumptions and engineering judgements that require verification or further definition through process and technology development activities. This document takes off from the TWRS Process Flowsheet to identify and prioritize tasks that should be completed to strengthen the technical foundation for the flowsheet.

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1.0 INTRODUCTION

The Tank Waste Remediation System (TWRS) Process Flowsheet (Orme 1995) was revised and re-issued in August, 1995. The flowsheet, which depicts a tank waste processing and disposal concept, complies with the commitments of the renegotiated Tri-Party Agreement (Ecology et. al. 1994), and reflects the process requirements that were in effect at the time of publication. The mass balance was modelled on ASPEN PLUS¹, a steady state flowsheet modeling program, using bases and assumptions as stated in Section 3.0 of the TWRS Process Flowsheet and in other guidance from TWRS top-level management (Alumkal 1994). Decisions on implementation of the flowsheet are pending.

Some of the assumptions that went into the mass balance calculations were "best engineering judgement." Therefore, substantiation of these "soft" assumptions is needed to validate the flowsheet. Demonstration of processes through testing is very costly and not always the best approach. When sufficient information is available, the preferred approach to validation is through engineering analysis. Testing is useful when the basis for engineering is weak, or when the chemistry of a process is complex and unpredictable. The objective of this document is to identify and prioritize information deficiencies so that development testing and engineering analysis in support of the TWRS Process Flowsheet can be targeted effectively.

A secondary objective is to anticipate additional process requirements that might be incorporated into the flowsheet at a later date, and identify technology development to respond to those requirements. "Out-of-scope" technology needs are addressed very briefly. These requirements could be as simple as an additional ion exchange separation, or as complex as acid dissolution of sludges and acidic solvent extraction separations processes.

Current tank farm operations (salt-well pumping, evaporation, waste consolidation and safety related activities for day-to-day operations) are outside the scope of this document. This document focuses on the retrieval, pretreatment, low-level waste treatment and high-level waste treatment technology needs mandated by the Tri-Party Agreement for the period of time beginning in 2003 and ending in 2028.

¹ASPEN PLUS is a trademark of Aspen Technology, Inc.

2.0 SUMMARY AND PRIORITIZATION OF TWRS FLOWSHEET DEVELOPMENT NEEDS

The twenty four page Process Flow Diagram (PFD) of the TWRS Process Flowsheet provides the framework for this study (See APPENDIX B). The PFD, in conjunction with a mass balance, predicts the flow of materials through the several operations. The reliability of this prediction is only as good as the bases used for the calculations; some bases are verifiable, others are more speculative until validated. The bases of the TWRS Process Flowsheet are found in APPENDIX A.

Mass balance bases for unit operations vary not only in quality, but also in significance. Some mass balance bases carry more weight than others in determining the results.

Each operation on the PFD received a subjective assessment of its maturity level and its potential for impacting the TWRS disposal mission. Impact levels, ranked either "2" or "1", indicate whether the item has the potential to be a "showstopper" at one extreme or an operational glitch at the other extreme. Impact level "2" items could cause the flowsheet to miss its objectives (e.g., achieving high waste loadings so a reasonable amount of HLW glass is produced), while "1" items could create an annoyance (e.g., misjudging the efficiency of an offgas scrubber so that filters have to be backwashed more frequently than anticipated).

Technical maturity levels are ranked from "A" to "C", "A" being a more technically mature element of the flowsheet. A maturity level of "A" indicates that the item is developed or nearly developed, engineered and ready for design, "B" indicates developed with little engineering or experience to support it, and "C" indicates promising but still in development. A "2C" item is one of high consequence with unresolved questions, i. e., a high-priority item.

Table 2-1 lists process flowsheet needs generally in descending order of priority, although no attempt is made to prioritize items with the same ranking. In some cases a considerable number of flowsheet concerns are consolidated into the items listed in the table. Section 4.0 defines the needs in more detail.

It is not the intention of this document to be a detailed technology development plan, but to direct attention to technology items that are important for validating the TWRS Process Flowsheet.

Table 2-1. TWRS Process Flowsheet Priority List

Impact Level	Technical Maturity	Item	Major Areas of Concern
2	C	High-Level Waste Loading	Verify high waste loading in glass; major assumption for reducing glass volume.
2	C	Process Feed Characteristics and Composition	Physical properties of solids, particle size, etc... Physical properties of slurries, viscosity, solids loading. Reliability of inventory, solubility data.
2	C	Rapid and on-line analysis for process control	Viability of quick turnaround analysis and online process control for high throughput, low holdup process. On-the-fly verification of glass quality.
2	C	Enhanced Wash Efficiency	Verify efficiency of settle/decant clarification and times cycles. Verify solubility, leach efficiency and rates.
2	C	LLW Melter	Melter reactions, melt retention, and offgas composition (especially volatiles - iodine, chlorine, fluorine, Tc).
2	C	Cl/F Control Process	Laboratory verification of modelling calculations. Radionuclide behavior.
2	B	Quench Flume	Control of cullet characteristics. Mature in industry.
2	B	HLW Melter	Melter reactions, melt retention, offgas composition, feed pretreatment, and glass product constraints.
2	B	Tank Integrity	Corrosion, erosion, temperature cycling, mechanical fatigue, cold brittle fracture, etc.
2	B	Cesium Ion Exchange	Characteristics of media chosen and secondary waste streams. Efficiency, stability of resin. Cost/benefit of a second cycle. Spent resin disposition.
1	B	Feed Adjustment Reactors	Additional components in waste not found in NCAW.
1	B	LLW Storage Air	Check for validity of pneumatic transfer.
1	B	Sulfur Cement Formulation	Composition specifications are robust.
1	B	Solids and Volatile Removal From Offgas	Simple, robust process. Verify efficiencies.
1	B	Operation of Frit Filter	Viability and efficiency of frit filter. Other filter types, filter media, filter aids and filter rejuvenation?
1	B	Disposition of Secondary Wastes	Non-vitrifiable waste components (HCl drums), miscellaneous solid wastes.
1	B	Reactions Between Wastes	Adverse affects after mixing retrieved waste.
1	B	HLW Centrifuge	Efficiency (data could be used for implementation of centrifuges in pretreatment).
1	B	LLW Roll Crusher	Impacts amount of recycled fines.
1	B	Process Condensate	Define conditions for reuse in retrieval.
1	A	LLW Feed Evaporator	Composition of overheads. Characteristics of bottoms.
1	A	HLW Evaporator	Composition of overheads.
1	A	Supernatant Evaporator	Composition of overheads.
1	A	Cesium Ion Exchange Evaporator	Composition of overheads. Not as important because overheads are recycled directly back to process.
1	A	LLW Cullet Screen	Mature process in industry.
1	A	Cyclone Operation	Mature process in industry.

Impact Level	Technical Maturity	Item	Major Areas of Concern
1	A	Pressure Swing Absorption	Mature process in industry.
1	A	SO ₂ Removal	Mature process in industry.
1	A	NO _x Destruction	Mature process in industry.
1	A	Claus Reactor	Mature process in industry.
1	A	Solids Blending	Mature process in industry.

Impact Levels:

Items designated "2" have major impact on flowsheet results.
 Items designated "1" have minor impact of flowsheet results.

Technical Maturity:

Items designated "C" are promising but still in development.
 Items designated "B" need adaptation for this application.
 Items designated "A" are common industrial practice.

3.0 SUMMARY OF THE TWRS PROCESS FLOWSHEET

The Tank Waste Remediation System (TWRS) process entails characterizing, retrieving, treating and disposing of 238,000,000 kgs (not including water) of chemicals contained in 149 Single-Shell Tanks and 28 Double-Shell Tanks. Using a variety of simple separations, the waste is segregated into a low activity fraction containing the bulk of the non-radioactive constituents, and a high activity fraction containing a relatively small percentage of the non-radioactive constituents. The low activity fraction is vitrified and disposed of on the Hanford site. The high activity/TRU fraction is stored in underground tanks until the HLW treatment facility is operational. The HLW is vitrified and stored on site pending removal to a national geologic repository. Melter selection is in progress. For the purposes of this flowsheet, a combustion fired LLW melter producing glass cullet is assumed. LLW cullet is packaged with a binder in large containers, and disposed of in vaults. The binder is tentatively identified as a sulfur polymer cement. Evaluation of other alternatives is in progress. The HLW process is based on a high-temperature, joule heated, liquid fed ceramic melter.

The process uses large amounts of water for retrieving and transferring waste to processing facilities. Water is recycled extensively within the process. Water that cannot be recycled or reused is treated and released to the environment. Offgases generated during vitrification are scrubbed, filtered, treated for criteria pollutants and released to the environment.

An overall process flow diagram (PFD) and mass balance are located at the end of Section 3.0. Detailed PFDs are provided for convenient reference in APPENDIX B. Readers requiring a more detailed process description are referred to the TWRS Process Flowsheet (Orme 1995).

The flowsheet will be revised as development work and technology selection in support of the TWRS mission progress. The flowsheet reflects pretreatment requirements as currently defined; other requirements may be added in later revisions. The LLW and HLW treatment as well as the LLW disposal depicted in the flowsheet are a tentative reference process.

3.1 CHARACTERIZATION

For the first revision of the TWRS Process Flowsheet, a tank-by-tank inventory was developed. The inventory, separates tank waste into two categories: the components that are in solution (the solubles) and the components that are not in solution (the insolubles).² The rationale for the separation is explained in APPENDIX A of the TWRS Process Flowsheet. The new tank inventory basis not only supports the TWRS Process Flowsheet, but provides a starting point for making decisions about retrieval sequence, blending, and evaluating the effect of feed variability.

²The inventory accounts for dilution during retrieval. Water was added to each tank to yield a 5M Na solution, or a 10 wt% solids slurry, whichever required more water.

Most of the 238,000,000 kgs of chemical inventory in the tanks is water soluble. There are 175,000,000 Ci of radioactivity, virtually all of it attributed to ⁹⁰Sr, ¹³⁷Cs and their daughter products.

Table 3-1. Summary of Major Constituents in Hanford Tank Waste

Soluble		Insoluble	
Component	Mass (kgs)	Component	Mass (kgs)
Al(OH) ₃	6.99E+6	Al	2.31E+6
Cl	6.78E+5	Bi	2.52E+5
CO ₃	3.10E+6	Ca	1.45E+5
Cr(OH) ₃	4.46E+5	Cancrinite	2.70E+6
F	1.14E+6	Ce	2.35E+5
Fe	3.44E+4	CO ₃	1.09E+5
K	7.07E+5	Cr	1.60E+5
Mn	1.08E+4	Fe	7.62E+5
Na	6.80E+7	Na	7.77E+5
NO ₂	9.47E+6	Ni	2.06E+5
NO ₃	1.07E+8	NO ₃	9.85E+5
OH	1.43E+7	OH	5.63E+6
PO ₄	3.20E+6	PO ₄	1.85E+6
SO ₄	2.02E+6	Si	2.32E+5
TOC	1.06E+6	UO ₂	1.54E+6
UO ₂	1.06E+5	ZrO ₂ ·2H ₂ O	1.20E+6
SubTotal	2.17E+8	SubTotal	1.91E+7
Other	1.0E+6	Other	6.0E+5
Total	2.18E+8	Total	1.97E+7
Radionuclides (Ci, decayed to 12/31/1999)			
⁹⁰ Sr/ ⁹⁰ Y	1.88E+6/1.88E+6	⁹⁰ Sr/ ⁹⁰ Y	5.17E+7/5.17E+7
¹³⁷ Cs/ ^{137m} Ba	3.19E+7/3.03E+7	¹³⁷ Cs/ ^{137m} Ba	3.01E+6/2.86E+6
Other	4.13E+4	Other	2.12E+5
Total	6.60E+7	Total	1.09E+8

3.2 RETRIEVE WASTE

The complexities of simultaneously operating multiple retrieval systems to retrieve 177 discrete batches of waste are outside the scope of this document. The TWRS Process Flowsheet does not "flowsheet" the retrieval operation, per se, but rather assumes the retrieval of 100%³ of the tank waste into a composite feed stream. This approach does not account for retrieval inefficiencies and day-to-day variability, but nonetheless serves the purpose of the flowsheet, which is to establish a conservative reference mass balance and overall throughput requirements.

The tank-by-tank inventory incorporated into Revision 1 of the TWRS Process Flowsheet allows the modelling of special cases. Groups of tanks or selected tanks can be "retrieved" and composited into a feed stream for process modelling.

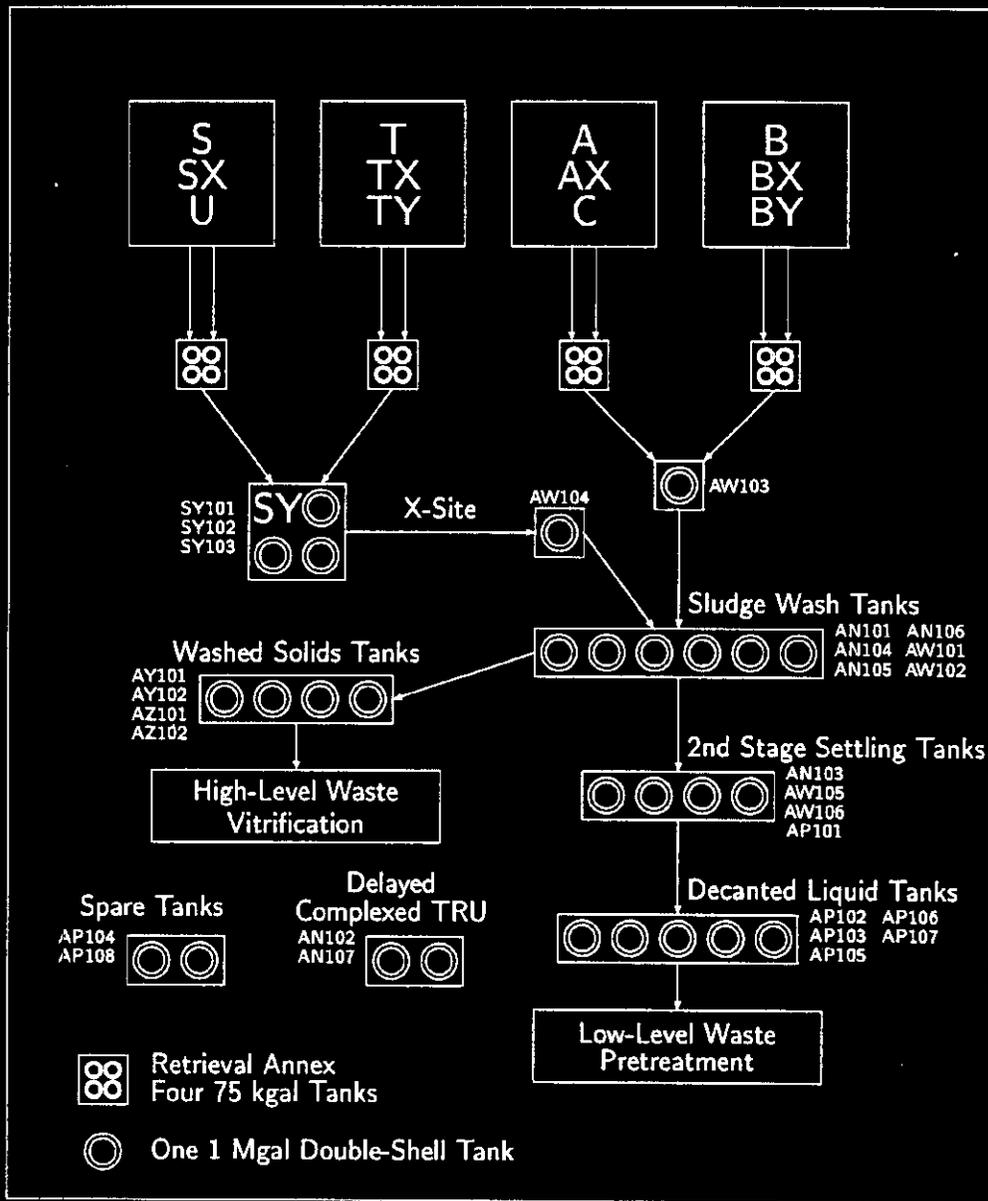
Of the possible methods (hydraulic, mechanical, or pneumatic) for mobilizing and retrieving tank waste, hydraulic methods (sluicing and mixer pumps) are assumed as the primary systems since they have been successfully demonstrated in similar applications, and are compatible with the underground pipe transfer system available at Hanford.

DST waste is retrieved by mobilizing with mixer pumps and transferring with standard DST transfer pumps. Mixer pump systems are not capable of completely removing solids from tanks, so there will always be a residual inventory of solids in DSTs that handle solids. This is not a disadvantage for day-to-day operations, but final cleanout of the DSTs will probably require supplemental retrieval methods.

SST waste is retrieved by sluicing from the SSTs to one of four Retrieval Annexes. In the Retrieval Annex, waste is conditioned as necessary to prepare slurries for long-distance transfers, and transferred by pipeline to in-process storage/treatment facilities. Figure 3-1 is a high-level schematic diagram of the tank farm configuration for waste retrieval operations and in-tank sludge washing.

³Eventually, waste will be retrieved from DSTs and SSTs to the extent required for closure. The closure requirements have not been fully specified. (Note: The TPA conditions for closure are that residues in 100 series tanks shall not exceed 360 ft³ and in 200 series tanks shall not exceed 30 ft³, but if the retrieval technology is capable of better, then the limit of the technology is required. Further decontamination of the tanks may be required to satisfy closure requirements).

Figure 3-1. Configuration for Retrieval and In-Tank Sludge Washing ⁴



⁴ Note that this is a configuration for in-tank sludge washing, not the configuration or the design. These tank assignments have not been optimized or even analyzed for feasibility. This configuration is being used for sequence modelling studies (Certa 1995). These assignments are subject to change pursuant to feasibility and advanced process design studies.

3.3 TRANSFER WASTE

The movement of waste from tank to tank and from tank to treatment facility is by pipeline transfer. The construction of new pipelines for retrieving waste is inherent in the Retrieval Annex concept. Cross-site transfer lines are required for movement of waste from 200 West to 200 East for processing. Other pipeline enhancements may be required to facilitate movement of waste to and from the treatment facility, and between DST farms.

3.4 STORE IN-PROCESS WASTE

Figure 3-1 tentatively identifies the SY Tank Farm for in-process storage of 200W Area waste. Two DSTs are identified for staging waste to the in-tank sludge wash process. Six DSTs are identified for enhanced sludge washing, four for 2nd stage settling, five for decanted liquids, and four for washed solids; while these are process tanks, they can also be viewed as in-process storage. Transfers to the treatment complex originate from the AP Tank Farm for decanted liquids, and later from the aging waste tanks for HLW.

In-process storage of other liquids is provided in theory (i.e., is indicated on the PFDs) to ensure continuity of operations, but the sizing of that storage is a process design issue. The other types of in-process storage include evaporated decanted liquids and Cs-depleted liquids.^{5 6}

The volume of pretreated HLW accumulated before the December 2009 startup of the HLW vitrification plant will depend on the tank retrieval sequence and schedule. In-process storage and blending of HLW is expected to occupy the tanks of the AY and AZ Tank Farms.

⁵ In-process storage of pretreated liquids should be avoided because of the equipment requirements to provide that storage. It would require one dedicated line to carry pretreated liquid to storage, dedicated tanks to store the waste, and another dedicated line to carry the stored waste to vitrification. The preferred approach, close-coupled operation of ion exchange and LLW vitrification, presupposes that an adequate combination of on-line process control and out-of-spec glass rework can be provided more cost effectively than in-process storage for pretreated liquids.

⁶ The TPA startup of the LLW vitrification plant lags the startup of LLW pretreatment by 6 months. Even at a reduced production rate for startup, the pretreatment process is capable of generating millions of gallons of pretreated waste, for which minimal in-process storage is available. Therefore the actual startup date of LLW vitrification must be 6 months ahead of the TPA schedule. The shortage of in-process storage between ion exchange and LLW vitrification requires that these units start up simultaneously.

3.5 PRETREAT WASTE⁷

3.5.1 Enhanced Sludge Washing

Enhanced sludge washing is assumed to be adequate to achieve an acceptable volume of HLW. A simplified diagram of the in-tank enhanced sludge washing sequence is shown in Figure 3-2. Retrieved solids are washed four times: First Wash (i.e., caustic leach), Second Wash, Third Wash and Fourth Wash. The last three are dilute caustic washes. During leaching and washing the tanks are agitated with mixer pumps. Each wash is preceded by settling and decanting to remove liquids and concentrate the solids. Supplemental 2nd Stage Settling is allowed for decanted waste liquors in case solids are entrained during 1st Stage decanting. A detailed process flow diagram (PFD) for in-tank pretreatment is depicted on Sheets 1 and 2 in APPENDIX B.

Figure 3-1 depicts the flow of materials through the in-tank process for a "strawman" tank farm configuration. Figure 3-1 tentatively identifies the tanks of the AN and AW tank farms for the bulk of the in-tank processing. The AP farm is set aside for the accumulation of supernatants and wash waters⁸ (LLW Pretreatment feed). The actual tank farm process has not been designed.

Batches of waste are retrieved into sludge wash tanks, settled and decanted until a $\sim 1.3E+6$ L batch of 20 wt% settled sludge is accumulated. The sludge is then digested in caustic. After a period of settling, the leach liquors are decanted. The leached solids are washed in three consecutive washes with a dilute caustic solution to remove the interstitial liquids.

Enhanced sludge washing takes advantage of the amphoteric property of certain waste components ($Al(OH)_3$ and $Cr(OH)_3$) to leach them from the solids. It also exploits the relative solubility of certain compounds to metathesize PO_4^{3-} from the solids. A fraction of the sodium in waste solids is also removed by leaching.

Batches of leached and washed solids are combined and blended in the washed solids tanks.

⁷ For some waste liquids containing high levels of complexed Sr and TRU, in-tank pH adjustments, in-tank chemical additions, and in-tank digestion at elevated temperatures may be warranted, but requirements for such treatment have not been defined for this flowsheet.

⁸ The distinction between Figure 3-2 and Figure 3-1 is important. Note that Figure 3-2 depicts a series of process steps, but not necessarily a process design or flow of materials. (The PFDs in APPENDIX B also diagram process steps). Figure 3-1, on the other hand, depicts a "strawman" tank configuration that has been modelled to evaluate tank retrieval sequences (Certa 1995). The concept in Figure 3-1 designates six tanks for sludge washing, with no movement of sludges between process steps, and four tanks for 2nd Stage Settling.

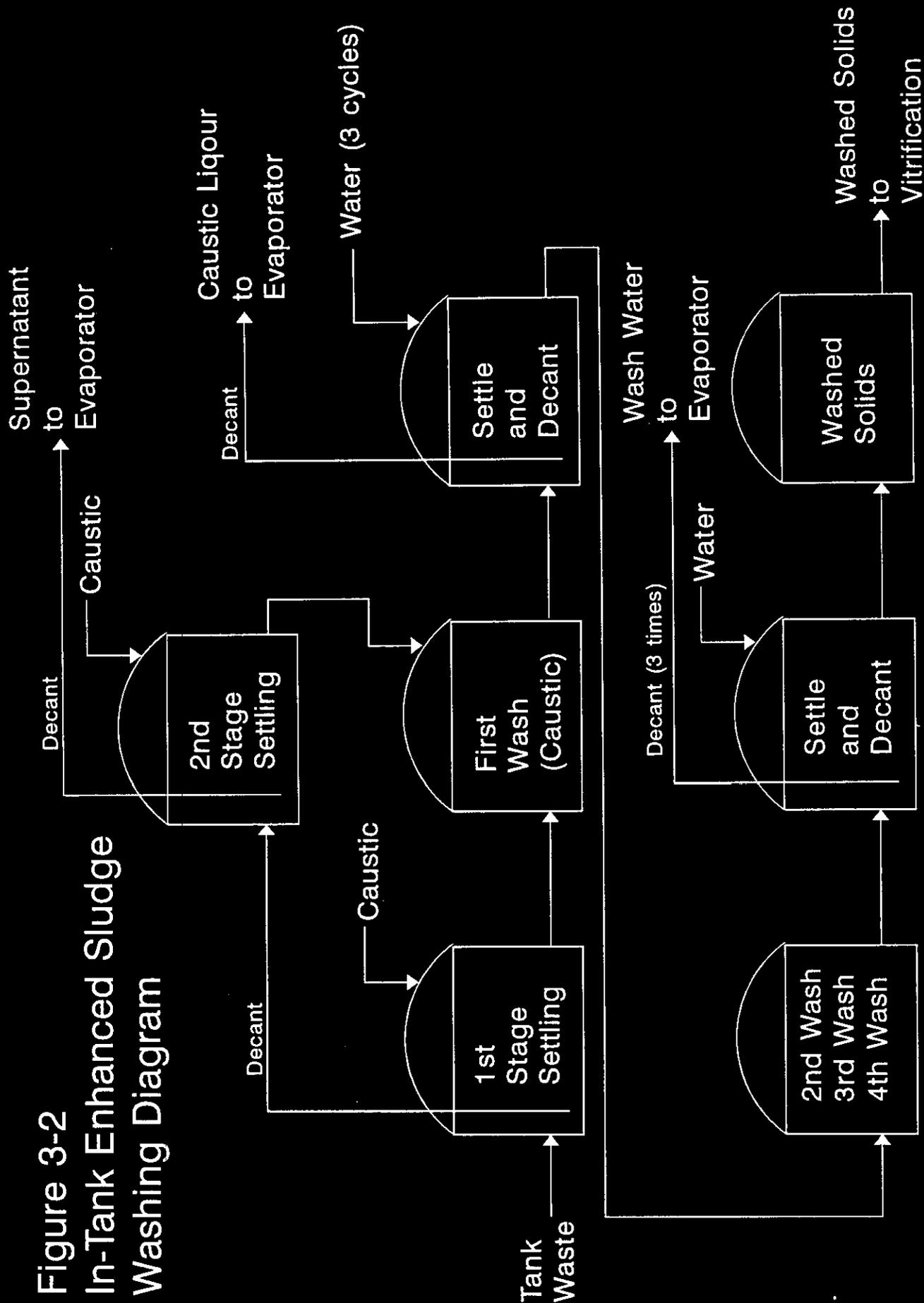


Figure 3-2
In-Tank Enhanced Sludge
Washing Diagram

3.5.2 Ion Exchange Feed Preparation

Decanted waste liquors, leachates and wash liquors from enhanced sludge washing are combined, concentrated to a uniform molarity by evaporation, and clarified in a deep bed frit filter. For design purposes, the evaporator bottoms are 7M Na. A detailed PFD for ion exchange feed preparation is depicted on Sheet 3 in APPENDIX B.

3.5.3 Ion Exchange

Cesium is separated from the clarified liquids by ion exchange. The purpose of ion exchange is two-fold: (1) produce a cesium concentrate stream that reduces the amount of material going to HLW vitrification, and (2) produce a cesium-depleted stream that satisfies LLW vitrification feed specifications. There is an aqueous makeup system, two ion exchange systems (each consisting of two ion exchange beds in series), and an evaporator. A detailed PFD for ion exchange aqueous makeup and ion exchange operation are depicted on Sheets 24 and 4 in APPENDIX B, respectively.

The ion exchange cycle consists of loading, elution and regeneration. Loading continues until the cumulative Cs loss through the second bed approaches the product specification. The system is designed so that the lead bed is in equilibrium with the feed (i.e., is fully loaded with Cs) before switching to the other system. The secondary bed is partially loaded. During loading, the maximum bed volumes per hour consistent with these conditions is dependent on the properties of the ion exchange resin.⁹ Therefore, the size of the ion exchange beds is also dependent on resin selection.

When fully loaded with Cs, the resin in the lead bed is eluted with nitric acid and then regenerated to the Na-loaded form. The partially loaded bed becomes the lead bed of that system, and the freshly regenerated bed becomes the secondary bed.

The Cs-depleted effluent, containing on average less than 1 Ci of ¹³⁷Cs per cubic meter of 5M Na solution (equivalent to an average 4 Ci/m³ of glass at 25 wt% Na₂O loading), is well below the Class C limit for waste disposal.

Ion exchange resin is replaced periodically because of deterioration in performance. Resin in its final cycle is eluted to remove cesium. The resin is fluidized and combined with Cs-depleted waste. The resin is oxidized in the LLW melter.¹⁰

⁹ Ion exchange is modelled in this flowsheet using a resin that has the properties of Rohm and Haas CS-100. This does not constitute an endorsement of CS-100. It is an engineering judgement that the properties of CS-100 provide a conservative basis for ion exchange design. Other ion exchangers continue to be developed and tested.

¹⁰ This disposition of spent resin is a major assumption at this point in time. Compatibility with the LLW glass making process has not been demonstrated.

3.5.4 Cesium Product

Cesium eluate is concentrated by evaporation of water and acid; the acidic condensates are recycled for use in subsequent elutions. The Cs concentrate is neutralized with caustic and stored in the DSTs. The Na/Cs ratio of the Cs concentrate should be significantly lower than the Na/Cs ratio in the ion exchange feed.¹¹

3.6 IMMOBILIZE LLW

The ion exchange effluent and several other recycled dilute process waste streams are combined and concentrated by evaporation. LLW immobilization is by vitrification in a high capacity, high temperature, combustion-fired melter. (Specification of a combustion-fired melter is tentative pending the results of a formal melter technology evaluation and selection activity). The vitrified waste is quenched with water and roll crushed to produce a glass cullet waste form. (Specification of a glass cullet waste form is tentative pending results of a formal waste form selection activity). The cullet is accumulated and air dried in bins in a cullet storage facility. Offgas treatment includes quenching, removal of particulates and SO_x , and reduction of NO_x . Recovered sulfur oxides are reduced to elemental sulfur and used for LLW disposal. Revision 1 has added a new operation to recover chloride and mercury from the offgas quench water. The recovered chloride is a new secondary waste stream. The PFD for LLW immobilization is depicted on Sheets 5, 6, 7, 8 and 9 in APPENDIX B. Treatment of the offgases is shown on Sheets 10, 11, 12, 13, and 14. The chloride removal process is on Sheet 23.

3.7 DISPOSE OF LLW

Specific TPA and internal technical direction is currently limited to requiring that the LLW be disposed of in glass and in a retrievable form. For this flowsheet, the dried LLW glass cullet is mixed with a remeltable sulfur polymer cement binder, cast in 32 m³ disposal containers, and transported to a near surface facility (disposal vault) for onsite disposal. (Specification of sulfur cement as the binder is tentative pending determination of the need for a binder and evaluation of other binders). The sulfur polymer cement operation is depicted on Sheet 8 in APPENDIX B.

3.8 IMMOBILIZE HLW

The feed to HLW immobilization is a combination of washed solids, spent filter frit, and Cs concentrate. (The feed may eventually include long-lived radionuclides (e.g., ⁹⁹Tc) recovered from the LLW or from the offgas of the

¹¹ For example, if the ion exchange feed has Na/Cs = 100,000 then Na/Cs = 1,000 in the Cs concentrate represents a 100 fold reduction in the amount of Na going to HLW.

LLW vitrification process if dictated by future separations requirements). The washed solids and spent filter frit are dewatered in a vertical centrifuge to reduce the evaporation load on the feed adjustment reactors. The centrate contains some solids and sodium (from NaNO_2 and NaOH added for corrosion control during interim storage of washed solids in the DSTs); the centrate is concentrated by evaporation and recombined with the dewatered solids before combining with the Cs concentrate. The HLW is processed through a feed adjustment reactor before vitrification in a joule heated, liquid fed ceramic melter. The vitrified waste is poured into steel canisters and cooled. The canisters are sealed, decontaminated, and transported to an interim storage facility awaiting removal to a geologic repository. Feed adjustment offgas is condensed to recover Hg. Melter offgas treatment includes quenching to recover volatiles, scrubbing to remove particulates, and HEPA filtration. Condenser vent gases are also scrubbed. The process flow diagram for immobilization of HLW is depicted on Sheets 15 and 16 in APPENDIX B. Treatment of the offgases is shown on Sheets 17, 18 and 19.

3.9 STORE HLW

Interim storage of the HLW canisters on the Hanford site will be addressed in a future release of the flowsheet.

3.10 MISCELLANEOUS PROCESS COMPONENTS

The process condensate recycle system is depicted on Sheet 20 in APPENDIX B. Essential material flows are summarized on Sheets 20, 21 and 22.

3.11 MATERIAL BALANCE VALUES and DESIGN RATES

To avoid confusion during design, the TWRS Process Flowsheet reports the total mass of each stream rather than flow rate. Design rate is specified independently of the TWRS Process Flowsheet through Design Requirements Documents (DRDs) and other design guidance provided to the architect engineering firm. Design rate takes into account not only the mass and duration of processing, but the type of operation (batch, semi-continuous, continuous), how operations interface with each other, and the total operating efficiency (TOE). TOE is the product of an availability factor (fraction of the time operating) and a capacity factor (average fraction of design rate achieved). Availability factor accounts for system induced downtime (shortage of feed, lack of product space) and all other reasons for downtime (maintenance, failures, work stoppages).

Design rate also accounts for the level of confidence in the flowsheet assumptions. For pretreatment operations, there is little uncertainty about the volume in and out. For vitrification, on the other hand, there is uncertainty about the waste loading that is achievable. For vitrification, higher design rates account for the uncertainty.

Table 3-2 provides a summary of total mass in key process streams.

Table 3-2. Summary of Key Process Streams ^a

	Stream #	Liquid Mass (kgs)	Solid Mass (kgs)	Comments
Enhanced Sludge Washing				
Feed	1	7.26E+08	1.97E+07	
Washed Solids	34	1.60E+08	1.39E+07	
Filtrates	101	1.07E+09	1.85E+05	
Evaporator				
Condensates	105	4.22E+08		
Bottoms	106	6.41E+08	1.85E+05	
Ion Exchange				
Feed	205	6.41E+08	1.85E+03	LLW product includes spent resin.
Cesium Product	230	1.15E+07		
LLW Product	233	7.22E+08	7.46E+05	
Evaporator				
Condensates	403	1.14E+09		
Bottoms	404	5.10E+08	1.52E+07	
LLW Melter				
Waste Feed	406	5.31E+08	1.94E+07	
Dry Adds	407		2.98E+08	
Glass	411		4.30E+08	
LLW Disposal				
Glass	437		4.21E+08	
Sulfur Cement	450		1.33E+08	
Evaporator				
Condensates	308	1.35E+08		
Bottoms	309	2.98E+07	1.67E+05	
HLW Melter				
Feed	313	5.63E+07	2.53E+07	
Glass	344		2.41E+07	

^aStream numbers are keyed to the Process Flow Diagrams in APPENDIX B.

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4.0 SHEET-BY-SHEET DISCUSSION OF TWRS PROCESS FLOWSHEET DEVELOPMENT NEEDS

The technical development needs reviewed in this section pertain to the bases and assumptions used to create the TWRS Process Flowsheet material balance (Orme 1995). A detailed listing of the material balance assumptions is provided in APPENDIX A. The following discussion addresses six aspects of each development need:

- Scope
- Objective
- Timing
- Justification
- Flowsheet Impact
- Recommended Approach

The scope section gives a brief description of the need and, in some cases, the assumptions used in the flowsheet. The objective section is a concise "problem statement" that defines the need. The "problem statements" are brief; subsequent planning activities are expected to fill in the details. For example, one of the needs for the flowsheet is the chemical and radionuclide inventory for all tanks. The objective section states the need, but it will not identify the analyses or the analytes. That will be determined by the end user of the information working in cooperation with the individual(s) who characterize the waste. The timing section usually identifies the activity for which the need is a predecessor. The time could be based on milestones (i.e., TPA, DOE, etc...) or relative to other technology needs. The justification section defines why the action is important. Flowsheet impact is a statement of how the flowsheet is affected by the information (or lack of information). For example, the reconciliation of a need could lead to alterations in the process flowsheet itself (e.g., the addition/deletion of process equipment). The recommended approach section describes generically how the need should be rectified.

For a clearer understanding of how these needs relate to the TWRS process, the reader is referred to the 24 sheet process flow diagram in APPENDIX B.

4.1 RETRIEVAL

The TWRS Process Flowsheet does not address waste retrieval technology per se. Instead, all tank waste is composited into a flowsheet feed stream for the purpose of quantifying the overall size of the tank waste disposal project.

The TPA, however, requires the development of SST retrieval sequences in parallel with the demonstration and implementation of SST retrieval technology. The retrieval sequences must define tank selection criteria, estimated retrieval schedules, and retrieval methods for each tank. The initial retrieval sequence document is due September, 1996 followed by an annual update.

4.1.1 Retrieval Scenario

Scope

The retrieval scenario must accommodate the requirements of privatization. Retrieval should be laid out in a way that minimizes the variations to the LLW and HLW melter feeds while simultaneously holding the volume of glass to an acceptable amount.

Start-up times for the processing facilities will also guide retrieval. The Westinghouse Hanford Company (WHC) recommendation is to couple pretreatment and LLW treatment and build this facility first. The HLW treatment facility will then be brought online after the pretreatment/LLW facility has been in operation. Therefore, retrieval should be setup so that the early start of pretreatment/LLW facilities does not overtax the available in-process storage.

Safety issues may have a controlling voice in the retrieval scenario. Retrieval sequences driven by safety considerations may produce larger volumes of immobilized waste. The impact of safety considerations should be determined and compared to increases in cost and operation time.

Objective

Define retrieval scenarios that produce acceptable volumes of product, meet all safety constraints, comply with TPA and privatization guidelines, and minimize the amount of additional tank space necessary.

Timing

Critical input for TPA milestone M-45-02A (initial SST retrieval sequence document), due September, 1996. Certa (1995) published a preliminary retrieval scenario that will be refined during FY 1996.

Justification

Presently the TWRS process flowsheet does not account for variability in retrieved waste, but processes all waste as a homogeneous mixture at a concentration of 5M Na. The flowsheet conditions are ideal in terms of feed variability and the amount of HLW glass produced. Feed variability from sequential retrieval can cause from 10 to 100 percent increase in HLW glass volume.

Flowsheet Impact

Altering the feed to the flowsheet through sequential retrieval will increase the amount of HLW produced. LLW volumes should be unaffected by the retrieval scenario.

Recommended Approach

Define retrieval sequences that comply with safety constraints, TPA guidelines, privatization requirements, and other tank selection criteria, and then test the sequence using the Baseline Simulation Model (BSM) for Hanford Tank Waste (Wittman et al. 1995). The BSM is capable of tracking a wide variety of performance measures for evaluating sequences. Retrieval scenario work is integrated with the process flowsheet to ensure consistency of modeling assumptions.

4.1.2 Characteristics of Sludges, Salt Cake and Slurries

Scope

The physical characteristics of sludges and salt cake (e.g., shear strength, rate of dissolution, density, viscosity, wt% dissolved solids, wt% undissolved solids, particle size) are important considerations in developing retrieval and mobilization systems, as well as slurry transfer systems. Retrieved waste slurries typically contain finely divided particles. The physical characteristics of particles and agglomerates of particles, and their concentration can control the rheology of these slurries.

Objective

A data base of sludge and slurry physical characteristics is a prerequisite to the conservative design of retrieval/mobilization systems and pipelines. Understanding the rheology of waste slurries will also be important for dealing with retrieved waste that falls outside the acceptable envelope, thus requiring special handling or pre-transfer conditioning (e.g., size reduction, concentration adjustment). The conditioning of retrieved waste to produce a transferable slurry may add requirements to the retrieval and transfer functions not currently anticipated.

Timing

The cutoff date for input into project W-320 is already past. Project W-320 resolves the high-heat safety issue in tank C-106 and provides a full-scale demonstration of sluicing technology. The project for final cleanout of C-106 goes into design in 10/97 (startup 7/02). The project for the initial SST retrieval project goes into design in 10/98 (startup 12/03). Mobilization demonstration of NCAW sludge begins in May, 1996, with sludge washing scheduled for 1999. Consolidation of TRU sludge begins with the installation of mixer pumps in SY-102 the last quarter of 1997, and in AW-105 the last quarter of 1998. Efforts at physically characterizing sludges and slurries should be consistent with these dates.

Justification

This task provides a technical basis for retrieval and transfer design. Development work completed during FY 1995 indicates that waste sludges and

slurries are capable of unexpected behavior and unpredictable rheology (Rector and Bunker 1995).

Flowsheet Impact

The characteristics of sludges at the individual tank level may dictate special retrieval requirements that affect material balances.

Recommended Approach

Core sample characterization should include measurements that meet the needs of retrieval system engineers.

4.1.3 Reactions Between Tank Wastes

Scope

Neither the TWRS Process Flowsheet or the Baseline Simulation Model accounts for chemical reactions that might occur through the combination of dissimilar wastes. Adverse reactions, such as the solubilization of TRU, copious precipitation resulting in more HLW sludge, and precipitation resulting in high viscosity slurries, should be avoided. This task could be considered an extension of the existing tank farm waste compatibility program (Sutey 1995)

Objective

Develop criteria to identify wastes that should not be mixed because of the potential for adverse consequences.

Timing

Work could be performed in parallel with the identification of retrieval scenarios and flowsheets.

Justification

Incidental chemical reactions during retrieval and waste transfers could compromise operations and adversely affect production schedules if occurrences are frequent.

Flowsheet Impact

Precipitation of solids could increase the volume of HLW and affect time cycles.

Recommended Approach

Perform a literature study to identify the potential chemistry problems of mixing dissimilar wastes, and verify by chemical modeling and/or laboratory

testing. Based on the retrieval scenario, determine the potential for adverse reactions and the extent of the adverse consequences. Criteria should be developed for identifying wastes that are not compatible. The adverse reaction chemistry could be added to the retrieval sequence model.

4.1.4 Water to Waste Ratio

Scope

The amount of water added during retrieval and transfer operations will depend on the method of retrieval as well as operating restrictions on the slurry transfer. Slurry density, viscosity and solids loading should be maximized while taking into consideration the cost and complexity of transfer projects that require bigger pumps, more booster stations, etc. Presently in the flowsheet model, the feed is an average 3 percent solids.

In the flowsheet, chemicals are assumed to be solubilized to the extent listed in Table 4-3. In real life, waste will not retrieve homogeneously from tanks; solids loading up to 10 percent is expected.

Objective

Define method of retrieval and specifications for cross site transfers (limiting component, solids content, etc...).

Timing

Completed after TPA milestone M-45-01 (Develop SST retrieval technology).

Justification

Water addition for retrieval is based on nominal 5 molar sodium in retrieved waste. Suggested changes for this factor have ranged from 7 to 0.5 molar. Method of retrieval could have an impact on the system if it adds more water than is needed for transfer.

Flowsheet Impact

Impacts downstream processing equipment sizing and LLW lag storage requirements.

Recommended Approach

Determine through laboratory analysis or past practice operations the average amount of water needed to retrieve saltcake and sludge individually. Using these values, calculate the amount of water needed to retrieve each tank. Compare the retrieval results to restrictions for cross site transfers and determine which is limiting. From this a water to waste ratio for each tank can be calculated.

4.2 FEED TO PROCESS

The waste feed stream, composited from individual tank inventories, directly impacts the volume of process streams, and the final volume of LLW and HLW. There are fewer DSTs than SSTs, and they are generally easier to sample and characterize. The difficulty of reconstructing SST inventories is illustrated by the disparity between recent LANL estimates of SST inventory and the long-established Hanford Defense Waste EIS estimate (Shelton 1995).

4.2.1 DST Waste

Scope

DST inventory is based primarily on laboratory data supplemented by process knowledge and information from fuel records. The inventory for the TWRS Process Flowsheet is summarized in Table 4-1. There are potential pitfalls with the current DST inventory. Several DSTs contain solids that have not been sampled. These solids are presumably precipitated salts that will redissolve upon retrieval, although this assumption has not been verified. The composition of unsampled liquids is generally inferred from similar waste. A good DST inventory becomes more important as the program moves toward specific waste processing plans.

Objective

Update the chemical and radionuclide inventory of each waste tank as new data becomes available. Account for the influx of salt well liquors and the movement of waste during evaporator operations.

Timing

Critical input for TPA decision M-50-03 (Evaluation of enhanced sludge washing). More immediately, the DST inventory supports the planning of privatization work scope.

Justification

Current inventory data is potentially deficient as noted above. The inventory also changes periodically due to tank farm operations.

Flowsheet Impact

The DST inventory contributes to the total inventory which drives process capacity requirements and final glass volumes.

Recommended Approach

DST inventories are updated from existing process records, and periodically from new analytical results. Several parallel efforts are in

progress at Hanford, so there should be a good basis for cross checking inventories from various sources.

Table 4-1. DST Chemical Inventory

Component	Soluble (MT)	Insoluble (MT)	Total (MT)
Al ⁺³	1.24E+03	3.32E+02	1.57E+03
Bi ⁺³	2.23E+00		2.23E+00
Ca ⁺²	1.01E+01	1.56E+01	2.57E+01
Cl ⁻	2.71E+02	1.37E+00	2.72E+02
CO ₃ ⁻²	1.48E+03	7.04E+01	1.55E+03
Cr ⁺³	4.63E+01	3.86E+01	8.49E+01
F ⁻	3.47E+02	4.20E+01	3.67E+02
Fe ⁺³	8.08E+00	1.54E+02	1.62E+02
K ⁺	5.37E+02	2.72E+01	5.64E+02
Mn ⁺⁴	7.68E+00	1.58E+01	1.36E+01
Na ⁺	1.10E+04	2.35E+02	1.12E+04
Ni ⁺³	4.07E+00	6.87E+00	1.09E+01
NO ₂ ⁻	3.00E+03	8.40E+00	3.01E+03
NO ₃ ⁻	7.45E+03	4.30E+01	7.49E+03
OH ⁻	2.92E+03	1.09E+03	4.01E+03
Pb ⁺⁴	1.89E+00	4.31E+00	6.20E+00
PO ₄ ⁻³	2.13E+02	2.14E+01	2.37E+02
Si ⁺⁴	1.55E+01	2.18E+02	2.34E+02
SO ₄ ⁻²	3.90E+02	3.61E+00	3.94E+02
Sr ⁺²			
UO ₂ ⁺²	9.25E+00	3.36E+01	4.28E+01
Zr ⁺⁴	4.90E-01	3.05E+02	3.05E+02
TOC	5.97E+02	7.21E+01	1.06E+03

4.2.2 SST Waste

Scope

SST inventory is based primarily on reconstruction of historical records and process knowledge. Extensive work has gone into developing a new approach for SST inventories (Agnew 1995). The fill history of most tanks can be documented; independent corroborating sample data is relatively sparse. The

bulk inventory results of the Agnew study are compared to previous inventory values in Table 4-2.

Table 4-2. Comparison of LANL Chemical Inventories with the 1985 EIS

COMPONENT	LANL (MT)	85' EIS (MT)	LANL/85' EIS
Al ⁺³	5.26E+03	2.96E+03 ^(a)	1.78
Bi ⁺³	6.64E+02	2.61E+02	2.54
Ca ⁺²	5.36E+02	1.28E+02	4.18
Cancrinite	1.94E+03	2.70E+03	0.719
Cl ⁻	3.50E+02	4.15E+02	0.843
CO ₃ ⁻²	2.73E+03	1.66E+03	1.64
Cr ⁺³	7.47E+02	2.68E+02 ^(b)	2.79
F ⁻	5.39E+02	8.12E+02	0.663
Fe ⁺³	2.59E+03	6.31E+02	4.10
K ⁺	1.31E+02	5.53E+01	2.37
La ⁺³	4.01E+01	1.88E+00	21.3
Mn ⁺⁴	1.75E+01	1.20E+02	0.146
Na ⁺	2.97E+04	5.73E+04	0.513
Ni ⁺³	2.10E+02	2.03E+02	1.03
NO ₂ ⁻	5.57E+03	6.52E+03	0.852
NO ₃ ⁻	4.28E+04	1.00E+05	0.426
OH ⁻	1.70E+04	1.06E+04	1.60
Pb ⁺⁴	1.32E+01	2.83E+01	0.466
PO ₄ ⁻³	3.91E+03	4.73E+03	0.827
Si ⁺⁴	9.41E+01	1.45E+01	6.49
SO ₄ ⁻²	4.32E+03	1.65E+03	2.62
Sr ⁺²	1.57E+02	3.60E+01	4.36
UO ₂ ⁺²	1.92E+03	1.61E+03	1.19
Zr ⁺⁴	9.36E+01	3.82E+02	0.245
TOC	2.99E+02	4.73E+02	0.633
TOTAL	1.22E+05	1.94E+05	0.629

(a) Adjusted from 2.21E+03 MT in the 1985 EIS. Does not include aluminum found in cancrinite, 2NaAlSiO₄·0.52NaNO₃·0.68H₂O.

(b) Adjusted from 9.59E+01 MT in the 1985 EIS.

Objective

The disparity between the LANL bulk inventory estimate and the old EIS estimate should be reconciled. Until the numbers are reconciled, the TWRS Process Flowsheet Modeling group recommends the EIS inventory as a basis for modelling. Update the chemical and radionuclide inventory of each waste tank as new data becomes available.

Timing

Critical input for TPA decision M-50-03 (Evaluation of enhanced sludge washing). The SST bulk inventory is a significant driver of waste volume, and waste volume is a major consideration in process design. Because of the large disparity in several key components, reconciliation of the SST inventory should be a high priority.

Justification

Current inventory data is potentially deficient as noted above.

Flowsheet Impact

The SST inventory contributes to the total inventory which drives process capacity requirements and final glass volumes.

Recommended Approach

A formal peer review should be convened to reconcile the SST inventory. Parallel efforts are in progress at Hanford, so there should be a good basis for cross checking inventories from various sources. When the peer review has completed its work, the inventory used in the TWRS Process Flowsheet will be updated.

4.2.3 Water Solubility of Tank Wastes

Scope

The above inventories are used in conjunction with solubility factors to calculate the partitioning of waste components between liquid and solid phases. Table 4-3 shows the calculated percentage of chemical components in solution after retrieval (i.e., the feed to pretreatment) for several DST waste types. The estimate is refined as new sources of data are generated and as methods for interpreting the data are improved. Solubility factors for SSTs have also been derived from core sample and other data (Colton 1995). A compilation of washing data from 27 SSTs, available at the time the flowsheet was issued, was incorporated into the solubility factors.

Table 4-3. Solubility Factors for Single Shell and Double Shell Tank Wastes

	CC	NCAW	NCRW	PFM	SST		CC	NCAW	NCRW	PFM	SST
Ag ⁺	0%	9%	0%	0%	0%	Ni ₂ Fe(CN) ₆	0%	0%	0%	0%	0%
Al ⁺³	95%	48%	9%	13%	25%	NO ₂ ⁻	99%	97%	81%	99%	99%
Am ⁺³	95%	2%	0%	0%	10%	NO ₃ ⁻	99%	99%	64%	99%	99%
As ⁺⁵	0%	36%	0%	99%	0%	Np ⁺⁴	0%	15%	0%	99%	10%
B ⁻³	95%	27%	0%	99%	0%	OH ⁻	93%	64%	18%	99%	78%
Ba ⁺²	90%	3%	0%	2%	0%	Pb ⁺⁴	0%	7%	0%	0%	0%
Be ⁺²	0%	7%	0%	1%	0%	PO ₄ ⁻³	99%	92%	0%	63%	50%
Bi ⁺³	0%	0%	0%	0%	25%	P ₂ O ₅ :24WO ₂ :44H ₂ O	0%	0%	0%	0%	0%
Cancrinite					0%	Pu ⁺⁴	95%	4%	0%	0%	2%
C-14	0%	95%	20%	0%	99%	Rb ⁺	0%	96%	0%	0%	0%
Ca ⁺²	90%	3%	2%	1%	5%	Re ⁺⁷	0%	11%	0%	99%	0%
Cd ⁺²	0%	0%	0%	2%	50%	Rh ⁺³	0%	14%	0%	0%	0%
Ce ⁺³	0%	6%	0%	0%	1%	Ru ⁺³	0%	9%	0%	99%	0%
Cl ⁻	99%	96%	97%	98%	95%	Sb ⁺⁵	0%	3%	0%	0%	0%
Cm ⁺³	0%	2%	0%	0%	1%	Se ⁺⁶	0%	39%	0%	0%	0%
Co ⁺³	0%	6%	0%	99%	0%	Si ⁺⁴	0%	43%	20%	6%	0%
CO ₃ ⁻²	99%	83%	80%	?	90%	Sm ⁺³	0%	1%	0%	0%	1%
Cr ⁺³	95%	91%	2%	35%	10%	Sn ⁺⁴	0%	0%	0%	0%	25%
Cs ⁺	99%	97%	50%	98%	75%	SO ₄ ⁻²	99%	99%	44%	99%	98%
Cu ⁺²	0%	5%	0%	0%	0%	Sr ⁺²	95%	1%	0%	0%	1%
F ⁻	99%	97%	93%	99%	95%	TcO ₄ ⁻	0%	81%	57%	99%	50%
Fe ⁺³	95%	0%	0%	0%	1%	Te ⁺⁶	0%	8%	0%	99%	0%
Hg ⁺²	0%	0%	0%	0%	99%	Th ⁺⁴	0%	5%	0%	0%	1%
I ⁻	0%	47%	20%	99%	99%	Ti ⁺⁴	0%	3%	0%	0%	0%
K ⁺	99%	93%	78%	99%	0%	Tl ⁺³	0%	6%	0%	0%	0%
La ⁺³	90%	1%	0%	0%	1%	UO ₂ ⁺²	95%	61%	0%	5%	5%
Li ⁺	0%	8%	0%	?	0%	V ⁺⁵	0%	36%	0%	0%	0%
Mg ⁺²	90%	2%	0%	0%	0%	W ⁺⁶	0%	0%	0%	0%	0%
MnO ₂	95%	0%	0%	0%	5%	Zn ⁺²	90%	21%	0%	0%	0%
Mo ⁺⁶	95%	94%	0%	18%	0%	Zr ⁺⁴	0%	0%	0%	0%	0%
Na ⁺	99%	97%	72%	90%	99%	ZrO ₂ :2H ₂ O	90%	0%	0%	0%	5%
Nb ⁺⁵	0%	0%	0%	0%	0%						
Ni ⁺³	95%	0%	0%	0%	0%						

Objective

Periodically update the solubility of individual chemical/radionuclide components for each tank as new data becomes available.

Timing

Verification of solubility data is a continuing effort that proceeds in concert with core sample characterization and waste pretreatment studies. Critical input for TPA decision M-50-03 (Evaluation of enhanced sludge washing).

Justification

Although a number of DST Tank Characterization Reports became available during the last year, the bulk inventory information therein provided few new insights into waste solubility. For DST waste (except for SY-101 and SY-102), solubility factors haven't been revised in over two and a half years. The solubilities currently in use for SSTs are based on experience with a limited number of tank samples (Colton 1995). Since new data becomes available periodically, revising solubility factors is an ongoing task.

Flowsheet Impact

The solubilities of several key components can have a dramatic impact on the TWRS Process Flowsheet. The main impact is on volume of HLW. Also if key components (Sr, TRU, etc) are more soluble than what is assumed, additional processing steps may be needed in order to insure that the LLW will meet disposal requirements.

Recommended Approach

Core samples should be processed in such a way that water solubility of the components can be determined. Debugging of thermodynamic models (e.g., ESP by OLI) should continue to provide an engineering tool for calculating solubility.

4.2.4 Feed to Process

Scope

Presently the feed to the TWRS Process Flowsheet is a homogeneous mixture of both the DST and SST wastes. The inventories listed in Tables 4-1 and 4-2 plus the solubility factors given in Table 4-3 are employed to derive the feed to the process. This composition is defined as the optimal feed to the process because it minimizes the volume of HLW produced. The next step is to develop methodology to estimate the feed from the retrieval of specific tanks.

Objective

Define actual feed composition(s) and characteristics (wt% solids, viscosity, density, etc...) using assumed retrieval sequences and currently available waste-specific data.

Timing

Work can be initiated immediately where reliable tank inventory data is available. For other tanks, it will be necessary to extrapolate solubility data from tanks of similar origin.

Justification

The average feed composition currently used for the flowsheet does not account for the variability that will result from sequential retrieval.

Flowsheet Impact

Impacts to flowsheet range from increases in tank storage requirements to a one hundred percent increase in final HLW volume.

Recommended Approach

As data becomes available pertaining to tank waste inventory and chemical solubility factors, retrieval scenarios will be determined. The output of these scenarios will be modeled through the TWRS Process Flowsheet model to determine the impact on the volume of wastes produced. However it should be understood that retrieval scenarios will not be determined by this alone. Safety issues, tank space requirements, and start-up times for the HLW and LLW processes will also be used to determine the retrieval scenario.

4.3 TANK FARM PROCESSING

Sheets 1 and 2 of the Process Flow Diagram (APPENDIX B) depict in-tank processing. Retrieved waste slurries are settled (1st stage settling tanks), decanted, and settled a second time (2nd stage settling). The decanted liquids comprise part of the feed to LLW pretreatment. The balance of the LLW feed comes from caustic washing of the settled solids and three water washes of the leached solids. This process is somewhat idealized. Development work during 1995 showed that the basic process will require modifications for some wastes, such as repeated caustic washings at elevated temperature, to extract the most benefit from the treatment.

4.3.1 Effectiveness of Enhanced Wash

Scope

The current flowsheet model employs sodium hydroxide to solubilize additional amounts of aluminum (68%), chromium (64%), phosphate (74%), and sodium (25%) subsequent to the initial settle-decant operation. These values are the average over all tank wastes (Orme 1995). Enough caustic is added to arrive at 3 molar NaOH solution and 8 wt% solids slurry in the product stream from caustic washing.

Objective

Determine the effectiveness of the enhanced wash for each waste tank at operating conditions, recommend alternate processing conditions based on the history of the waste. If speciation information is available for solids, that should also be considered.

Timing

Critical to TPA milestone M-50-03 (Evaluation of enhanced sludge washing).

Justification

The assumptions used for the effectiveness of enhanced washing are supported by data, but the data are limited. Also, the conditions at which the experiments were run (~100 °C) are out of range for the actual process (ambient conditions). The flowsheet is compensating for the lower flowsheet temperature by allowing more time for caustic leaching.

Recommended Approach

Testing should be conducted on actual tank wastes at expected operating conditions. The operating conditions may vary depending on the characteristics of the waste, similar to studies completed by PNL in late FY 1995 (Lumetta 1995). The study varied solution to solid ratio, caustic concentration, and temperature for wastes that didn't leach well under normal experimental conditions. The tanks chosen for testing should represent the expected range of sludge composition expected. A cost/benefit analysis should also be performed that compares the cost savings in HLW versus the increased cost in LLW with the varying amounts and concentrations of sodium hydroxide used.

4.3.2 In-Tank Solid/Liquid Separation

The TWRS Process Flowsheet does not currently use assumptions with respect to settling rate. It does use an empirically derived and generalized assumption with respect to the compaction of settled solids. Progress at understanding the parameters that control settling rate and degree of

compaction that began with FY 1995 studies (LaFemina et al. 1995a, LaFemina et al. 1995b, LaFemina et al. 1995c, Rector and Bunker 1995a, Rector and Bunker 1995b) should be continued as the program moves toward developing waste specific flowsheets. This understanding will enable engineers to project the effectiveness of in-tank settling and decanting operations.

4.3.2.1 Solid Settling Rates

Scope

The Aspen software supports only steady-state modeling so the current version of the TWRS Process Flowsheet does not address the duration of settling. The development work completed during FY 1995 made it clear that particle interactions and solution chemistry can affect settling rates greatly. Understanding settling rates provides a defensible basis for projecting time cycles.

Objective

Understand what parameters control particle agglomeration and consequently solid settling rates for a representative number of waste tanks using surrogate solutions and solids. Settling rates will be determined for the following conditions: after retrieval (based on retrieval specifications), after enhanced washing (based on enhanced washing specifications), and after dilute caustic washes.

Timing

Input to TPA milestone M-50-03A (Evaluation of advanced sludge washing processes) and to the design of in-tank sludge washing systems.

Justification

Present solid settling rates are based on limited data from a 1982 Savannah River Site demonstration, work with Hanford simulants and B Plant process testing. The parameters that control rate should be determined so the applicability of the work is general rather than tank specific.

Flowsheet Impact

Solid settling rates control process cycle times, and ultimately the number of settling tanks required to support the specified duration of the TWRS mission. A cost/benefit analysis may be indicated to determine whether more tanks or longer duration is more effective.

Recommended Approach

Potential parameters to study include the effect of flocculents, effect of liquid composition, effect of solids speciation, effect of initial solids

concentration, and effect of primary particle size distribution. When practical, surrogate studies should be confirmed with actual waste.

4.3.2.2 Degree of Solids Compaction

Scope

The TWRS Process Flowsheet makes a general assumption that solids settle to 20 weight percent with minimal solids carryover in the decantates. The development work completed during FY 1995 made it clear that particle interactions and solution chemistry can affect the degree of compaction.

Objective

Understand what parameters control the compaction of solids during settling, especially how to scale up laboratory results to full-scale tank operations. Degree of compaction should be determined for the following conditions: after retrieval (based on retrieval specifications), after enhanced washing (based on enhanced washing specifications), and after dilute caustic washes.

Timing

Input to TPA milestone M-50-03A (Evaluation of advanced sludge washing processes) and for process design.

Justification

Degree of compaction affects chemical usage and the number of washes, and therefore the time to complete sludge washing.

Flowsheet Impact

If solids compact less than expected, fewer solids can be accumulated per batch, bigger volumes of wash liquor are generated, and the extra processing burden taxes downstream operations (evaporation, ion exchange and vitrification). The total number of leach and wash cycles increases.

Recommended Approach

Compaction testing should be coupled with the testing performed in section 4.3.2.1 to understand settling rates. Settling processes and compaction are closely related and probably have a number of controlling parameters in common. A representative number of tanks should be tested using surrogate solutions and solids. Laboratory tests should be conducted in a way that simulates the static pressure effect of large scale settling.

4.3.2.3 Decanting Operation

Scope

In the flowsheet, the decanting operation removes supernate after the slurry has settled to 20 weight percent solids. The amount of solids carried over is 0.33 percent of the solids in the tank for each decant.

Objective

Determine degree of decanting possible for each step of operation. Also test methods for controlling decant operation that minimizes the amount of solids carryover.

Timing

Input to TPA milestone M-50-03A (Evaluation of advanced sludge washing processes).

Justification

Degree of decanting and solids carryover is based upon best engineering judgement.

Flowsheet Impact

The decanting operation has a direct impact on the volume of HLW produced and/or the number of decanting steps necessary to achieve the desired separation. Solids carryover could also adversely impact the assumptions for downstream equipment.

Recommended Approach

Couple work with work performed in sections 4.3.2.1 and 4.3.2.2. A turbidity meter or equivalent device could be employed to determine solids concentration versus height versus time. The actual mechanics of the decant operation will need to be determined in a separate study for it is beyond the scope of this one.

4.3.3 In-Process Storage Issues

Scope

In the flowsheet model, the mixing of waste liquors with leach and wash liquors is assumed to produce stable solutions. The dissolution of solids is also assumed to be complete after caustic leaching. The model does not account for reactions or physical changes occurring during in-process storage, or for slow liquid phase reactions occurring in decanted liquids.

Objective

Evaluate the potential for liquid waste instability. Verify that solids stored under flowsheet conditions (low caustic, low nitrate) remain mobile for the subsequent transfer to vitrification.

Timing

The potential for problems during in-process storage should be evaluated before commencing with final design.

Justification

The storage conditions for solids change dramatically as a result of pretreatment. Waste solids currently are exposed to highly caustic and salty interstitial liquids; after pretreatment the solids are exposed to relatively dilute solutions. Liquids from different sources are mixing and changing temperature during in-tank operations which changes the "equilibrium" achieved after many years of storage.

Flowsheet Impact

The flowsheet issue is the processability of liquids and solids as a result of unanticipated chemistry during in-process storage.

Recommended Approach

Liquid waste stability issues should be addressed in conjunction with Section 4.1.3 Reactions Between Tank Wastes. The storability of washed solids could be demonstrated by simple, long-term (up to 1 year) experiments.

4.3.4 Tank Integrity

Scope

In-tank processing will place demands on underground tanks that may not have been anticipated in their design and construction. Evaluation of the suitability of tanks for processing is an engineering activity, but the data to support the evaluation will come at least partially from development tasks.

Objective

Determine corrosion and erosion rates that will be typical of in-tank processing. Determine effects of frequent cycling of temperature, level, etc.

Timing

Input to TPA milestone M-50-03A (Evaluation of advanced sludge washing processes).

Justification

Use of tanks for in-tank processing is a major assumption of the reference case.

Flowsheet Impact

Assessment of tank integrity could impact the flowsheet in a number of ways. There could be constraints on the duration of usage, constraints on the frequency of operations, constraints on temperature cycling or other limitations that would require construction of new tanks.

Recommended Approach

Tank integrity analysis was initiated by the Retrieval Program to support the installation of mixer pumps in DSTs. These studies should be continued and expanded to evaluate the impacts of in-tank processing. Corrosion and erosion are the two areas that could be studied in the lab.

4.4 ION EXCHANGE FEED ADJUSTMENT SECTION

The feed adjustment section (Sheet 3) adjusts the feed to the cesium ion exchange section by evaporating it to a specific sodium molarity and removing solids from the evaporator bottoms.

4.4.1 Operation of Supernate Evaporator

Scope

The supernatant evaporator (EV-139) boils off water until the bottoms are a certain sodium molarity (7 M). Compared to operating the 242A Evaporator, operating the supernatant evaporator will have to be more streamlined and robust to support the high volume anticipated by the flowsheet. The flowsheet factors for entrainment in the overheads should be verified.

Objective

Verify overheads content for the evaporator. Develop, improve and validate easy-to-use thermodynamic models for high concentration salt solutions to facilitate predictions around the evaporator. The extent of evaporation will depend on feed specifications for the cesium ion exchanger. Determine if evaporator operations dissolve TRU, i.e., increases the solubility of TRU solids in the evaporator bottoms.

Timing

The overheads will need to be determined before the specifications for the condensate retention basin (Tk-806 Sheet 20) are made.

Justification

Overhead contents are currently based on best engineering judgement.

Flowsheet Impact

Changes in evaporator overheads may lead to additional treatment processes in the condensate treatment section. Also may lead to additional safety restriction in the condensate retention basin.

Recommended Approach

Collect and evaluate operations data from evaporators and obtain a correlation between their overhead and feed. The evaluation should attempt to discriminate between volatility and entrainment. Input this data to the flowsheet model to determine the impact on process condensate treatment. Once an evaporator is chosen for the facility, a surrogate solution can be used to determine the overheads more accurately. Continue efforts to validate thermodynamic models for high concentration salt solutions. Develop an operating philosophy that facilitates continuous operation.

4.4.2 Effectiveness of Supernatant Clarification

Scope

The frit filter (F-202) protects the ion exchange columns by removing solids that precipitated in the evaporator bottoms (and any carryover from the decant operation). There may be alternative clarification approaches. The alternatives need to be investigated and downselected to the "best" filter. Spent filter beds with their burden of collected fines are flushed out and combined with the pretreated liquids, implying that the solids entrained in decantates are insufficient to make decantates or spent filter material TRU waste. In other words, TRU separation is not a function of the filter.

Objective

Identify the characteristics of particles (e. g., particle size distribution, agglomeration behavior, and loading (grams/liter)) that would adversely affect ion exchange column operations. Determine the "best" filter to prevent plugging of the IX column. The "best" filter is defined as the filter that efficiently removes solids that could plug the IX column, produces the least secondary waste, is relatively simple to operate, is reliable, and has little potential to adversely impact downstream processing.

Timing

The filter selection should occur after the feed to it is well defined (Sections 4.1 - 4.3) and the specifications for the cesium ion exchange column are documented (Section 4.5).

Justification

The operating parameters of the filter are based on engineering judgement.

Flowsheet Impact

The filter operation has little impact on the mass balance, however, an improperly designed filter could greatly impact the operability of the process.

Recommended Approach

Document feed compatibility criteria for ion exchange, which then become the specifications for filter performance. Test filters with a variety of feeds against the compatibility criteria. If actual feeds are not available, ascertain if testing with simulants would be productive. Simultaneously determine the impact the filters may have on downstream processing (i.e., cesium ion exchange column, waste volumes produced, etc...).

4.5 CESIUM ION EXCHANGE SECTION

The cesium ion exchange section (Sheet 4) consists of cesium ion exchangers, a cesium ion exchange product concentrator, and the supporting tankage. The aqueous makeup facility for ion exchange is on Sheet 24. The cesium ion exchanger consists of two columns in series. While one ion exchanger is in the loading cycle, a redundant system is in the elution/regeneration cycle. The model accounts for the uptake of cesium and potassium. Other cations, such as calcium and strontium, are probably captured to a certain extent, but this has not been tracked in laboratory loading studies. The resulting cesium-depleted effluent from the columns is sent to LLW processing. When the loading cycle is complete, the ion exchanger is valved off and the regenerated ion exchanger is valved in. The cycle frequency will depend on actual system design and the nature of the feed on any given day, but typically a loading cycle lasts about 1 day. The resulting cesium rich stream is sent to the cesium ion exchange concentrator where water and nitric acid are boiled off. The bottoms are sent to HLW processing and the nitric acid stream is recycled to column elution/regeneration.

Development of criteria and acceptance tests for procuring IX media should be proceeding in parallel with the following process related development.

4.5.1 Operation of Ion Exchange Column

Scope

Although regenerative ion exchange is a common industrial operation, this particular application challenges the durability and performance of any ion exchange resin. The resin must survive frequent concentration swings that weaken its structure while maintaining an acceptable overall separation factor. Several aspects of the operation should be verified.

Objective

The following list of questions should be addressed when testing for a CsIX column:

- IX media to be used
- Efficiency of media to remove cesium
- Effect other chemicals have on capture efficiency (i.e., potassium, sodium, etc...)
- Removal of other components from the feed stream (i.e., strontium, TRU, etc...)
- Size and number of columns necessary
- Configuration of columns
- Life cycle of media
- Swelling of media during loading, elution, and regeneration
- Disposal of media
- Effect chemical additions (flocculent) have on column operation
- Resistance to plugging
- Amount and composition of regeneration/elution streams
- Efficiency of regeneration/elution streams
- Impact regeneration/elutions streams have on entire process
- Clumping of the ion exchange medium during loading, elution, and/or regeneration
- Degradation of ion exchange medium in radiation fields

Cesium removal efficiency, other cation removal, composition and amount of regeneration and elution streams (if necessary), and downstream impacts of fugitive ion exchange media are the main factors affecting the flowsheet model.

Timing

Critical to TPA milestone M-50-01-T02 (Start detailed design of LLW pretreatment facility).

Justification

Verification of flowsheet modeling for this unusual application of ion exchange would be prudent.

Flowsheet Impact

The main impact is postulated to be dependant on the elution and regeneration streams' compositions and amounts. The amount of acid needed for elution can lead to increased HLW volumes if the Cs concentrate stream has to be neutralized as the flowsheet currently shows. The flowsheet schematic itself may undergo revision if a different ion exchange media is selected.

Recommended Approach

The specific ion exchange media to be tested are the reference resin and any other promising developmental IX media under investigation in ongoing IX programs. However the selection process should use a surrogate with the composition given from the flowsheet model and the results should be directly coupled to the model in order to determine the impact on HLW and LLW volumes.

4.5.2 Operation of Cesium Evaporator

Scope

The cesium ion exchange concentrator (EV-224) is used to remove most of the water (99 percent) and nitric acid (70 percent) while leaving all of the cesium in the bottoms. The removal of the nitric acid is important because any acid left in the evaporator bottoms requires neutralization with caustic. The addition of caustic (sodium) increases the number of HLW canisters.

Objective

Determine the composition of the evaporator overheads and degree of nitric acid removal possible. The splits noted above agree with modeling calculations, but have not been verified empirically. Document the operational parameters used (i.e., temperature, pressure).

Timing

Timing is dependant on the CsIX column selection process. The possibility exists that as the selection process continues the need for the evaporator may be eliminated.

Justification

Operation based on best engineering judgement preliminary modeling.

Flowsheet Impact

If the evaporator cannot achieve the degree of nitric acid removal specified, the volume of HLW will increase.

Recommended Approach

First determine the need for the CsIX evaporator. If the need exists, use the thermodynamic capabilities of ASPEN PLUS to model an evaporator and obtain the operational parameters. Using the operation parameters found using ASPEN PLUS as a starting point, verify in the laboratory the degree of separation possible and the composition of the overheads. There is much B Plant and PUREX plant experience in evaporating nitric acid solutions.

4.5.3 Spent Resin Disposition

Scope

The flowsheet currently addresses resin replacement by dumping spent resin to the Cs depleted product stream which then becomes feed to the LLW melter. Conditions in the combustion fired melter volatilize and burn the organic portion of the resin; any metallic elements on the resin are incorporated in the glass. This disposition of old resin is highly speculative at this point, and possibly subject to invalidation if an alternative melter technology is selected. Non-combustion melters may not be compatible.

Objective

Evaluate the technical feasibility of in-melter resin destruction for the reference melter and two other front-running melter concepts. For the combustion melter, determine if resin can be substituted in kind for the fuel. For all melters, determine the adverse impacts, if any, on melter operation. Determine the adverse impacts, if any, on glass product quality.

Timing

This flowsheet issue should be closed before the start of pretreatment facility detailed design.

Justification

The current flowsheet should not be rejected until it is definitively shown that in-melter resin destruction is untenable. The alternatives to the flowsheet are not attractive -- drumming out large amounts of resin or ashing resin both require additional processing operations.

Flowsheet Impact

The impacts to the flowsheet if the reference approach does not work are noted above.

Recommended Approach

The initial investigation into this question should be paper studies based on the best engineering judgment of knowledgeable experts and literature sources. The scope of the investigation could be expanded to examine the effect of feeding high-TOC complexed wastes to a melter, an issue that is not so different from the organic resin question.

4.6 LOW LEVEL WASTE FEED ADJUSTMENT, VITRIFICATION AND CULLET HANDLING

Sheets 5-7 depict the immobilization of LLW. The feed is mixed with recycle streams before it enters the LLW feed evaporator where it is concentrated. The bottoms from the evaporator are then combined with rework glass before feeding to the melter. In the melter, the waste dehydrates, melts and mixes with glass formers. The molten glass is then solidified via rapid quenching in water before proceeding to a roll crusher for size adjustment of the cullet. The resulting glass slurry is then pumped to a screen where it is washed with water to remove fines before being sent to LLW cullet lag storage. The glass slurry water, the wash water, and the glass fines accumulate in the LLW filter catch tank. Here, part of the water is filtered and recycled back to the quench flume. The balance of the water slurries the glass fines back to the LLW feed evaporator.

Cullet accumulates in lag storage, is air dried, and then pneumatically transferred to a cyclone where the cullet is separated from the transfer air and stored in a day bin. LLW glass product (rework) that is out of LLW specification is rerouted through a separate cyclone separator, crushed to fines, and recycled to the melter. From the day bin, the in-spec cullet feeds the glass-in-sulfur process.

4.6.1 Operation of LLW Feed Evaporator

Scope

The LLW feed evaporator (EV-402) concentrates the feed to a high sodium molarity (10 M). The feed is concentrated in order to decrease the load on the melter and melter offgas equipment. In the flowsheet, no precipitation occurs and the content of the overheads is determined by the factors in APPENDIX A.

Objective

Verify that the estimated contamination in the overheads is reasonable and develop or verify the modeling capabilities for high density salt solutions.

Timing

The overheads will need to be determined before the specifications for the condensate retention basin (TK-806 Sheet 19) are made.

Justification

Overhead contents are based on best engineering judgement. Solution models are developmental.

Flowsheet Impact

Changes in evaporator overheads may lead to additional treatment processes in the condensate treatment section (section 4.14); also, may lead to additional safety restrictions in the condensate retention basin. The characteristics of high density solutions may necessitate special handling requirements.

Recommended Approach

Perform a literature search of past evaporators and obtain a correlation between their overhead and feed. Input this data into the flowsheet model to determine the impact on the process condensate treatment section. Once an evaporator is chosen for the facility, a surrogate solution can be used to determine the overheads more accurately. Continue refinement of thermodynamic models for physical property prediction.

4.6.2 Control of Evaporator Feed

Scope

The total volume required for in-process storage of pretreated LLW has not been fixed. It will be dependent on the duration of the process control scheme that is eventually devised for qualifying feed to the LLW Feed Evaporator. The range of possibilities is from a minimal duration, in which case the in-facility holding tanks are adequate, up to 6 months duration, in which case up to 10 DST feed tanks would be required (Claghorn 1995). Current estimates show that if 0.5 percent of the LLW is made into out-of-spec glass, and routed to HLW, the amount of HLW glass will increase by approximately 10 percent. This illustrates the importance of good control on the feeds to LLW vitrification and that recycling off-spec LLW is mandatory.

Objective

Determine the data needs for controlling feed to LLW vitrification, how LLW melter feed will be characterized and length of time to perform such characterization.

Timing

Need will have to be addressed after TPA milestone M-51-02 (Selection of reference melter).

Justification

Flowsheet assumes that the feed to LLW is within specifications, but does not provide guidelines for how that control will be maintained.

Flowsheet Impact

Results have no impact on the flowsheet model, but could impact equipment sizing, throughput and other operational considerations.

Recommended Approach

After selection of the melter, feed specifications should be set (e.g., acceptable concentrations of radioactive and nonradioactive components). A preliminary document to define LLW analytical needs should give some indication as to the time needed for characterization (Shade et al.).

4.6.3 LLW Melter

Scope

The TPA states that the LLW fraction will be disposed of in a glass form. The melter in the LLW flowsheet is a high capacity, high temperature, combustion fired melter. See Appendix A for assumptions made for the LLW melter. Unfortunately, the Vortec-type melter probably will not be selected as the reference melter. Therefore the operational parameters used in the model will need to be altered.

Objective

The following questions need to be addressed for the LLW melter.

- Batch/continuous operation
- Formation of secondary phases
- Solids loss to overheads
- Retention of chemicals in melt
- Number/size of melters
- Additional chemicals to be added
- Methods of frit addition

- Final glass composition restrictions
- Additional up-front processing necessary

These are not all of the questions, but these are vital to the flowsheet model. The other questions lie beyond the scope of this document.

Timing

Objective will be defined when TPA milestone M-60-02 (Selection of reference melter(s)) is met.

Justification

Present LLW melter is modeled after a Vortec melter design.

Flowsheet Impact

Changing LLW melters has the potential to drastically alter the flowsheet model as well as the process schematic. The volume of glass produced will depend on the restrictions on the final glass composition, which can be affected by melter selection. Melt retention and offgas composition could change significantly, as well as the up-front processing.

Recommended Approach

The reference melter will be selected based on its ability to process the feed, but it will also be based on operational parameters that lie outside the scope of this document (i.e., melter life, operability, sensitivity, etc...). A surrogate(s) should be selected that represents the bounding feed to the melter. This surrogate will then be used to test the melter's ability to vitrify the LLW and form a product that meets all LLW restrictions. This melter testing progressed through Phase 1, but Phase 2 did not proceed due to the current emphasis on privatization. Melter selection will now fall within the privatized scope of waste disposal.

4.6.4 Operation of Quench and Roll Crusher

Scope

The quench flume and roll crusher are used to form the cullet from the molten glass. The flume uses water to solidify the glass and the roll crusher size reduces the glass to an acceptable mesh.

Objective

Consult with industry experts and then test quench flume operations to learn how to control cullet characteristics. Determine amount of quench water necessary and amount of fines produced. Similarly, test the roll crusher to determine characteristics of roll-crushed glass.

Timing

Quench flume and roll crusher will be tested after the melter and the melter feed (or surrogate) are selected.

Justification

Operation of a quench flume and roll crusher are mature in industry, but should be tested in conjunction with the melter and Hanford-type LLW glass.

Flowsheet Impact

The quench flume and roll crusher have the potential to increase the amount of fines produced. These fines will pass through the screen (FS-422) and will be recycled back to the melter feed. A large amount of recycle may decrease the throughput of the melter or cause line plugging problems.

Recommended Approach

Perform a literature search to determine what effect the quench water has upon the size of the cullet and the amount of fines produced by roll crushers. Consult with industry experts. From this data the type and operation of the quench flume and roll crusher can be determined.

4.6.5 Operation of Screen

Scope

The screen separates cullet and drops it to lag storage (B-427). The size of the cullet will be determined by the final disposal process and LLW disposal restrictions.

Objective

Determine operational parameters of the screen.

Timing

The screen is not a high priority item - timing is not critical.

Justification

Update flowsheet.

Flowsheet Impact

None.

Recommended Approach

Determine screen operational parameters after quench flume and roll crusher are chosen. This will define the feed to the screen. Also, cullet size restrictions for the glass in sulfur process will define the desired size of the cullet to be captured by the screen.

4.6.6 Operation of LLW Cullet Lag Storage

Scope

The LLW cullet lag storage bin (B-427) stores the cullet while it is being dried and analyzed. The design and sizing of the cullet lag storage bin will be determined by the process control requirements placed on the cullet, most notably the frequency of cullet sampling and the duration of the analysis.

Objective

Determine size and physical placement of cullet lag storage bin. Also determine if pneumatic is the best method for cullet transfer.

Timing

Input to TPA milestone M-50-01-T01 (initiate definitive design of LLW pretreatment facility).

Justification

The duration of product quality analysis could cause the cullet lag storage to be extremely large. Improving the turnaround of product quality samples could be a cost effective alternative to large lag storage facilities.

Flowsheet Impact

No direct flowsheet impact based on the size of the bin. The mechanism for cullet transfer could impact the flowsheet schematic however. Removal of pneumatic transfer and insertion of a physical transfer mechanism (i.e., screw conveyor, bucket conveyor, etc...) could remove the need for the downstream cyclone (FC-432) and associated filters.

Recommended Approach

Bin size and physical placement will depend on how long the cullet will need to be stored before proceeding to the final disposal process. This will be based on the length for analysis and the difference between the melter output and the final disposal input. This will be determined as the processes become more developed. A literature search should be conducted to determine the optimal method of cullet transfer from the bins. Comparisons should be

made based on the amount to be transferred, the distance travelled, the height lifted (if any), and additional equipment needed.

4.6.7 Operation of Cyclone

Scope

The cyclone (FC-432) separates the cullet from the transport air. The degree of separation is expected to be extremely high, but may be dependant on the mode of transport. Pneumatically transporting the cullet may cause a large amount of fines to be produced. If this is the case, the load on the sintered filters may be high. Presently the model assumes no fines are produced.

Objective

Determine operational parameters of cyclone and filters.

Timing

Work should be coupled with study to determine method of cullet transport (section 4.6.6).

Justification

Cyclone may be removed from flowsheet if superior alternatives for transporting cullet are identified.

Flowsheet Impact

Removal of cyclone from flowsheet schematic.

Recommended Approach

The need for cyclone will be dependant on the results from the previous section. A literature search will be conducted to determine the average amount and size of fines produced and the separation efficiency for the cyclone and associated filters.

4.6.8 Rapid to Real-Time Process Control

Scope

The supernatant pretreatment and LLW vitrification operation are in need of rapid and, if possible, real-time analytical methods to ensure in a timely manner that aqueous process streams and glass product quality are within specification. Antiquated methods of grab sampling and lengthy analysis were satisfactory for the way facilities were operated in the past, but have the potential to drive up the cost of waste treatment facilities significantly.

Objective

Develop approaches to process control that reduce the demand for large volumes of in-process storage.

Justification

The available methods of analysis are time consuming, resulting in the hold up of large volumes of waste while process control analysis tests are performed. Providing lag storage for large volumes of liquids and LLW glass is very expensive.

Flowsheet Impact

Without rapid process control capabilities, lag storage demands in the low level process line could become excessive.

Recommended Approach

Before development begins in this area, a process control philosophy should be defined so that the controlled parameters are understood, i.e., what is going to be measured and what is the envelope of acceptability? After the process control philosophy is established, then the development objectives can be defined.

4.7 SULFUR CONCRETE PROCESS

The sulfur concrete process (Sheet 8) packages the LLW cullet in a sulfur matrix. The cullet is fed from the day bin into the mixer (MM-440) where it is mixed with molten sulfur and oligomers (dicyclopentadiene and cyclopentadiene), and then deposited in 32 m³ containers. The sulfur concrete product is 30 vol% cement and 70 vol% cullet.

4.7.1 Sulfur Concrete Product

Scope

TPA and internal technical direction currently requires that the LLW be disposed of as glass in a retrievable form. For this flowsheet the LLW glass cullet is combined with a sulfur polymer cement binder in packages that are disposed of in vaults. The packages are retrievable; the sulfur concrete is remeltable if subsequent processing is called for. See Appendix A for specific assumptions.

Objective

Demonstrate the technical and economic viability of the sulfur cement waste form. Ensure that the final product will meet all applicable restrictions for LLW disposal including retrievability.

Timing

Input to TPA milestone M-50-01-T01 (initiate definitive design of LLW pretreatment facility).

Justification

Current extrapolations of literature data for the disposal of LLW in a sulfur cement only show that it is a promising alternative (Mullally 1994). Further testing is necessary to demonstrate its acceptability.

Flowsheet Impact

Presently the evaluation of LLW disposal alternatives is in progress. The selection of sulfur cement is tentative and may be changed in the future. Flowsheet impacts vary from altering the composition of the sulfur binder and/or cement product to substituting a completely different disposal process altogether.

Recommended Approach

The *Tank Waste Technical Options Report* (Boomer, 1993) evaluated several different LLW disposal options and settled on sulfur cement as the most promising. The sulfur cement must be tested for leachability, diffusivity, resistance to chemical attack and radiation, permeability, combustibility, and gaseous emissions among others. If the sulfur cement product does not prove to be a viable disposal process then another process will need to be selected and evaluated.

4.7.2 Sulfur Cement Equipment

Scope

Special safety considerations might need to be given to the sulfur cement equipment due to the elevated operating temperatures.

Objective

Test sulfur cement equipment for operability. Perform a safety risk assessment of the entire sulfur cement process.

Timing

Timing is dependant on selection of sulfur cement as the LLW disposal process (section 4.7.1). This section may be used in the evaluation of sulfur cement.

Justification

Process knowledge about the sulfur cement process is limited.

Flowsheet Impact

None.

Recommended Approach

Perform a literature search to determine the operational risks of the sulfur cement process. Contact users of the process to obtain their input.

4.8 LLW CULLET RECYCLE PROCESS

The cullet recycle process (Sheet 9) consists of a cyclone and a roll crusher. Off-spec cullet is pneumatically transferred from the cullet storage bins (Sheet 7) to a cyclone where the cullet is separated from the transport air. The cullet is then routed to a roll crusher where it is size reduced. Crushed cullet falls into the recycle cullet catch tank, is slurried with water back to the LLW melter feed tank (Sheet 5).

Scope

All process equipment used will be tested in other sections (cyclone - section 4.6.7, roll crusher - section 4.6.4). No additional technical needs are present.

4.9 LLW OFFGAS TREATMENT

The LLW offgas system (Sheets 10-11) consists of solids removal, SO₂ removal, and NO_x destruction processes. The solids removal process utilizes a quench tower, a venturi scrubber/separator, and a demister to remove solids from the melter offgas. A copper oxide absorber is then employed to capture SO₂ from the gaseous stream before it enters the NO_x catalytic reactor where the NO_x is reduced to elemental nitrogen and water.

4.9.1 Solids Removal from Offgas

Scope

The major purpose of the quench tower, venturi scrubber, and demister is to remove solids and water from the melter offgas stream. Simultaneously additional recovery of gaseous components (NH₃, Tc, Hg, etc...) will occur.

Objective

Determine solids and "others" removal efficiency from the melter offgas stream for each piece of equipment. Also test all equipment together in series to determine overall removal efficiency.

Timing

Testing will follow LLW melter testing in order to obtain a representative melter offgas composition.

Justification

Removal efficiencies used in the model are based on best engineering judgement.

Flowsheet Impact

Actual removal efficiencies may significantly change the solids burden on downstream HEPA filters, requiring either changes to the scrubber efficiency or to the filter design.

Recommended Approach

Perform a literature search to determine capture efficiencies for the equipment using the melter offgas from section 4.6.3. Include efficiencies for solids as well as the "others".

4.9.2 Operations of SO₂ Recovery Process

Scope

The sulfur dioxide recovery process removes the SO₂ from the gas stream so that it can be transferred to the Claus reactor for sulfur recovery and recycle.

Objective

Verify that SO₂ removal from melter offgas stream is sufficiently high enough to satisfy SO₂ emissions requirements.

Timing

Conduct testing after LLW melter tests. This data will be needed in order to determine how much removal is necessary.

Justification

Ensures emissions of SO₂ for the plant is below code.

Flowsheet Impact

Variations in SO₂ removal changes the feed to the Claus reactors and ultimately the amount of sulfur recycle to the sulfur cement process.

Recommended Approach

The SO₂ removal process is mature in industry. A literature search should determine operational parameters and removal efficiencies. Vendor testing could be employed in order to verify results.

4.9.3 Operation of NO_x Destruction Process

Scope

The NO_x destruction process reacts NO_x with ammonia at elevated temperatures to form nitrogen and water.

Objective

Determine NO_x destruction efficiency and operational parameters of the process.

Timing

Conduct testing after LLW melter tests. This data will be needed in order to determine how much removal is necessary.

Justification

Ensures emissions of NO_x for the plant is below code.

Flowsheet Impact

Changes amount of NO_x released.

Recommended Approach

The NO_x destruction process is mature in industry. A literature search should determine operational parameters and removal efficiencies. Vendor testing could be employed in order to verify results.

4.10 OFFGAS RELATED PROCESSES

4.10.1 Chlorine Control

Scope

A new addition to Revision 1 of the TWRS Process Flowsheet removes chlorine from the from the recirculating scrub solution. The process is depicted on Sheet 23.

Objective

This process has been modelled on ASPEN PLUS but no supporting empirical verification is currently available.

Timing

Verification tests should be successful before going to detailed design.

Justification

The process splits should be verified by testing. Also, materials testing is an important aspect of verifying this process because of the highly corrosive environment.

Flowsheet Impact

If the chlorine control line isn't viable, then the flowsheet has a serious, unresolved issue with the accumulation of volatile chlorine in the offgas system.

Recommended Approach

Verify through small scale laboratory simulation.

4.10.2 Operation of Claus Reactor Process

Scope

The captured SO_2 is stripped from the copper oxide bed (Sheet 11) and routed to a Claus reactor (Sheet 12) where it is reduced to elemental sulfur. The sulfur product is routed to the LLW sulfur cement process and the gas stream is recycled back to the copper oxide absorber.

The Claus reactor reduces the incoming H_2S and SO_2 to elemental sulfur.

Objective

Determine overall sulfur recovery efficiency and operational parameters.

Timing

Conduct testing after LLW melter and SO₂ recovery tests.

Justification

Based on best engineering judgement.

Flowsheet Impact

Variations in sulfur removal efficiency directly impact SO₂ removal efficiency because what is not recovered is recycled back to the SO₂ recovery process.

Recommended Approach

The Claus reactor process is mature in industry, although the cyclical nature of the flowsheet operation may introduce unique process control problems. A literature search should determine operational parameters and removal efficiencies. Vendor testing could be employed in order to verify results.

4.10.3 Vent Treatment System

The vent treatment system (Sheets 13-14) filters the process vents with HEPA filters prior to atmospheric release. Solids recovered from the vents are recycled back to the LLW evaporator feed tank (Sheet 5). Operation of HEPA filters is mature and will not require testing.

4.11 HIGH LEVEL WASTE FEED TREATMENT SECTION

In the HLW feed treatment section (Sheets 15-16) the feed is centrifuged and the supernate routed to an evaporator. In the evaporator the supernate is concentrated, then recycled back and mixed with the centrifuged solids. The melter feed is then combined with glycolic acid and glass additives before feeding to the melter. The molten glass from the melter is poured into canisters and allowed to cool before being sent to interim storage (eventually offsite to the repository for disposal).

4.11.1 Operation of HLW Feed Centrifuge

Scope

The centrifuge (Sheet 15) is utilized in conjunction with the evaporator in order to dewater the feed. Its purpose is to reduce solids loading in the evaporator.

Objective

Test centrifuge using characteristics of HLW feed. Determine separation efficiencies and operational parameters. Additional testing may require the addition of a flocculent.

Timing

Input to TPA milestones M-50-03 (decision whether advanced sludge separation processes are required) and M-51-03-T02 (initiate definitive design of HLW vitrification facility).

Justification

There have been mixed results with centrifuging waste solids in the past. (Results from this work may have broader application if, for example, centrifuges are proposed for sludge washing in some future modification of the flowsheet).

Flowsheet Impact

For the HLW feed treatment section the centrifuge is used in conjunction with the evaporator (section 4.11.2) to decrease the load imposed upon the feed adjustment reactors (FARs) (section 4.11.3). If it is concluded that the FARs can cope with the increased load, the evaporator and the centrifuge may be deleted from the flowsheet. However centrifuge development work may be continued depending on the need for centrifuges in the pretreatment section (section 4.3.5).

Recommended Approach

Test centrifuges using HLW feed surrogate. Centrifuge development may be coupled with flocculent work (section 4.3.2.2).

4.11.2 Operation of HLW Evaporator

Scope

The HLW evaporator (Sheet 15) is used to reduce the load on the FARs. Presently the evaporator removes approximately 80 percent of the incoming water. The overheads contain entrained components.

Objective

Determine composition of evaporator overheads based on FAR feed specifications. Simultaneously the need for the evaporator will be determined.

Timing

Input to TPA milestone M-51-03-T02 (initiate definitive design of HLW vitrification facility).

Justification

Overhead contents are based on best engineering judgement.

Flowsheet Impact

Changes in evaporator overheads may lead to additional treatment processes in the condensate treatment section (section 4.14). Also may lead to additional safety restriction in the condensate retention basin.

Recommended Approach

Perform a literature search of past evaporators and obtain a correlation between their overhead and feed. Input this data into the flowsheet model to determine the impact on the process condensate treatment section. Once an evaporator is chosen for the facility, a surrogate solution can be used to determine more accurately the overheads of it.

4.11.3 Feed Adjustment Reactors

Scope

The feed adjustment reactors (FARs) remove water from the melter feed stream to decrease the evaporative load on the HLW melter (Sheet 16). Also, all melter additions are performed here. The rheology of the melter feed slurry is also adjusted.

Objective

Determine composition of FARs overheads. Important issues around the FAR are mitigating hydrogen and ammonia evolution, rheology control, solids loading, simplicity of control, and adaptability to feed variations.

Timing

Input to TPA milestone M-51-03-T02 (initiate definitive design of HLW vitrification facility).

Justification

Overhead contents are based on best engineering judgement.

Flowsheet Impact

Changes in FAR overheads may lead to additional or modified treatment processes in the condensate treatment section (section 4.14). Also may lead to additional safety restriction in the condensate retention basin.

Recommended Approach

Perform a literature search of FAR technology to understand the current state of the art. Recent work at PNL with respect to FAR operations should be digested and applied to the TWRS Process Flowsheet (Seymour 1995).

4.11.4 HLW Glycolic Acid Additions

Scope

In the FARs the melter feed is combined with glycolic acid to volatilize mercury and to convert carbonate to carbon dioxide and nitrite to nitrogen oxide and nitrous oxide. More specific needs pertaining to feed preparation chemistry studies can be found in Roal 1994a.

Objective

Determine amount of glycolic acid to add and the reactions that occur within the FARs.

Timing

Work should be closely coupled with the determination of FAR overheads.

Justification

Parameters are based on work conducted at the Defense Waste Production Facility at Savannah River not on Hanford wastes.

Flowsheet Impact

Glycolic additions do not impact melter performance in the flowsheet model. Offgas treatment may be impacted by the acid additions.

Recommended Approach

Work with Savannah River to determine the reactions that occur and other reasons why the acid is added. Determine if the reasons that Savannah River adds the acid are applicable to Hanford's waste.

4.11.5 HLW Glass Former Additions

Scope

The amount and type of glass formers used are based on the glass specifications for the HLW product. Method of addition is based upon the melter type. More specific needs pertaining to glass formulation studies can be found in Roal 1994a.

Objective

Determine amount, composition, and method of addition for glass formers. There should be a heavy emphasis on minimizing additives to the glass so that waste loading in the glass is as high as possible.

Timing

Will be based on outcome of TPA milestone M-51-02 (selection of reference melter).

Justification

Amount and composition of glass formers presently used in the flowsheet model are based upon outdated Hanford Waste Vitrification Plant specifications.

Flowsheet Impact

Glass former specifications are based upon melter and HLW specifications. If these change, the glass former composition and amounts will change.

Recommended Approach

Glass former amounts, composition, and method of addition are all dependant on the type of melter selected. This must be kept in mind while the reference melter is being selected.

4.11.6 Control on HLW Melter Feed

Scope

The duration of melter feed laboratory analysis can affect or place limitations on the handling of washed solids. Duration affects the number of tanks required for accumulation and blending, and limitations on blending leads to less efficient waste loading in glass.

Objective

Determine how HLW melter feed will be characterized and length of time to perform such characterization.

Timing

Need will have to be addressed after TPA milestone M-51-02 (Selection of reference melter).

Justification

No rework is taken into account for the HLW section. The flowsheet assumes that all glass product meets the HLW specifications. In other words, the glass making process is certified rather than the product.

Flowsheet Impact

Results have no impact on the flowsheet model, but could impact equipment sizing and throughput.

Recommended Approach

After selection of the melter, the glass specifications should be set (e.g., acceptable concentrations of radioactive and nonradioactive components). Setting the analytical needs should give some indication as to the time needed for characterization.

4.11.7 HLW Melter

Scope

The HLW melter is modeled after a joule heated, liquid fed ceramic melter. The molten glass product from the melter is poured into steel canisters and cooled.

Objective

The following questions need to be addressed for the HLW melter.

- Batch/continuous operation
- Formation of secondary phases
- Solids loss to overheads
- Retention of chemicals in melt
- Number/size of melters
- Additional chemicals to be added
- Methods of frit addition
- Final glass composition restrictions
- Additional up-front processing necessary

These are not all of the questions, but these are vital to the flowsheet model. The other questions lie beyond the scope of this document.

Timing

Objective will be better defined when TPA milestone M-60-02 (Selection of reference melter(s)) is met.

Justification

Melter selection has not been finalized.

Flowsheet Impact

Changing HLW melters has the potential to drastically alter the flowsheet model as well as the process schematic. The volumes of glass produced will depend on the restrictions on the final glass composition, but these should not vary significantly. Melt retention and offgas composition should be independent of the melter selected, but up-front processing could vary significantly.

Recommended Approach

The reference melter will be selected based on its ability to process the feed to it, but it will also be based on operational parameters that lie outside the scope of this document (i.e., melter life, operability, sensitivity, etc...). A surrogate(s) should be selected that represent the bounding feed to the melter. This surrogate will then be used to test the melter's ability to vitrify the HLW and form a product that meets all HLW restrictions.

4.12 HLW OFFGAS SYSTEM

The HLW offgas system (Sheets 17-19) consists of a solids removal process that utilizes a quench tower, a venturi scrubber/separator, and a demister to remove solids from the melter offgas. Also included in the offgas system is a mercury trap, an ammonia destruction tank, a secondary waste evaporator, and an offgas scrubber. The flowsheet for the HLW offgas system was patterned after the Defense Waste Processing Facility and may be in need of some adjustments for processing Hanford waste. Alternate equipment may be more appropriate or streams could be rerouted.

During the preparation of this document, a labeling error was discovered on Sheet 19. The facility ventilation system is labeled "Storage Bin Vault" and it should say "Process Cell", i.e., the process cell of the HLW vitrification plant. The stack is likewise labeled "Cullet Storage Facility Stack ST-912" and it should say "Process Facility Stack ST-912". The LLW facility has its own Process Facility Stack ST-902.

4.12.1 Solids Removal from Offgas

Scope

The major purpose of the quench tower, venturi scrubber, and demister is to remove solids and water from the melter offgas stream. Simultaneously additional recovery of gaseous components (NH₃, Tc, Hg, etc...) will occur.

Objective

Determine solids and "others" removal efficiency from the melter offgas stream for each piece of equipment. Also test all equipment together in series to determine overall removal efficiency.

Timing

Testing will follow HLW melter testing in order to obtain a representative melter offgas composition.

Justification

Removal efficiencies used in the model are based on best engineering judgement.

Flowsheet Impact

Increased removal efficiency may lead to removal of redundant pieces of equipment while decreased removal efficiency may lead to insertion of additional pieces of equipment.

Recommended Approach

Perform a literature search to determine capture efficiencies for the equipment using the melter offgas from section 4.6.3. Include efficiencies for solids as well as the "others". HLW work should be coupled with the LLW solids removal work (section 4.9.1) to minimize redundancy.

4.12.2 Mercury Trap

The mercury trap concept originated in Savannah River where the mercury content of the waste is much higher. The need for a mercury trap in the TWRS Process Flowsheet should be evaluated further. Hanford waste contains relatively little mercury.

4.12.3 Ammonia Destruction

The operation parameters for the ammonia destruction tank (TK-601) must be determined. Also, the need for the destruction will be verified and optional stream routings investigated.

4.12.4 Secondary Waste Evaporator

The bottoms product from the secondary waste evaporator (EV-300) is currently routed back to the feed collection tank (Tk-315 Sheet 15). If the spent scrub solution was instead routed to the HLW feed evaporator (EV-311 Sheet 15) via the HLW evaporator feed tank (Tk-309 Sheet 15) the secondary evaporator could possibly be deleted.

4.12.5 Condenser Off-Gas Scrubber

The main purpose of the scrubber (SCRUB-1) is to remove residual amounts of mercury and ammonia from the melter offgas. Future flowsheet runs may determine that this is a redundant piece of equipment and should be deleted from the flowsheet.

4.12.6 Secondary Waste Recycle

In Revision 0 of the TWRS Process Flowsheet, the Salt Waste Holding Tank (Tk-603 Sheet 18) discharged secondary offgas wastes back to the tank farm, which purged the HLW system of potentially troublesome recycling materials. In Revision 1, to make the HLW plant a standalone facility, the secondary offgas wastes are recycled within the process. The impact of this change has not been fully evaluated, but deserves careful scrutiny in the future.

4.13 AUXILIARY PROCESS SYSTEMS

Beginning on Sheet 20, the PFD illustrates the auxiliary subsystems of the TWRS Process Flowsheet. These include the process condensate system, the pressure swing absorption facility for separating air into oxygen and nitrogen, the essential materials summary diagram, and the aqueous makeup facility for the ion exchange process.

4.13.1 Process Condensate

Scope

The process condensate system (Sheet 20) recycles water back to the process as necessary. Excess condensate is assumed to be sent to a liquid effluent treatment facility (LETF) for purification and ultimate release. The excess condensate could be diverted from the LETF and recycled back to the retrieval operation. No provisions are made for possible impacts the operation of the LETF might have on the TWRS Process Flowsheet. Process condensate composition will depend on evaporator operations.

Objective

Determine composition of condensate and if it can be recycled directly to retrieval operations. Determine size of effluent retention basins. Determine if LETF can process excess condensate and amount of secondary waste produced.

Timing

Evaluation can be made after process condensate composition is determined.

Justification

The model has a routing to the DSTs for off specification condensate, but assumes that there is none. Also no water is recycled for retrieval operations.

Flowsheet Impact

Using recycled water for retrieval operations would greatly reduce the need for fresh water, and also drastically reduce the amount of treated water discharged to the environment.

Recommended Approach

Using evaporator overhead compositions, determine if it is safe to use the recycle water for retrieval operations. Develop concepts for how condensates or treated condensates could be recycled for retrieval.

4.13.2 Pressure Swing Absorption Unit

Scope

The pressure swing absorption unit (PSAU) (Sheet 20) is utilized to obtain an enriched oxygen stream from atmospheric air. The reason for using the PSAU is two-fold; an enriched oxygen stream will decrease the overall load on the offgas equipment and the purchasing and storing of liquid oxygen can be decreased or eliminated.

Objective

Determine operating parameters based on the oxygen needs of the flowsheet. Insure that "off the shelf" PSAU's will meet the flowsheet needs.

Timing

Determination should occur after the oxygen needs for the flowsheet have been determine (order of magnitude only).

Justification

Operability based on vendor literature.

Flowsheet Impact

If the PSAU can not meet the needs of the flowsheet, liquid oxygen will need to be added.

Recommended Approach

Contact vendors to verify efficiency and throughput of PSAU.

4.13.3 Bulk Chemical Storage

Bulk chemical storage (Sheet 21) defines the raw material need for the process. No technical needs are present.

4.13.4 Glass Additive Formulation

Glass additive formulation (Sheet 22) is a blending operation to prepare the materials that will be added during the melting of LLW and HLW glasses. Formulation is dependant on melter feeds and product specifications. No technical needs are present.

4.13.5 Ion Exchange Aqueous Makeup

Sheet 24 depicts aqueous makeup of the streams for the water flushes, elution, and regeneration. There are no technology needs for this section.

5.0 DISCUSSION OF OUT-OF-SCOPE TECHNOLOGY DEVELOPMENT

Out-of-scope development includes potential areas of technology development not currently included in the TWRS Process Flowsheet, but that may be integrated into the flowsheet in the future if waste processing requirements change. TWRS Process Engineering has taken the position that out-of-scope development should consume no more than 20% of the total development resources, the balance of resources going to activities that directly support the TWRS Flowsheet (Roal 1994b). The list of these processes includes, but is not limited to:

- *Heat and Digest treatment for removal of Sr and TRU from solutions
- Thermal Reconstitution studies
- Physical Separations of Sr and TRU from solutions
- Inorganic Ion Exchanger testing
- Selective Sludge Leaching testing
- Sludge Dissolution studies (acid)
- Radionuclide Separations (acid)
- *Ion Exchange treatment to remove Tc
- Bulk Chemical Separations
- Chemical Recycle

Some of the above processes are applicable to only a few waste tanks or specific waste types. The above items indicated by an asterisk, in the judgement of the authors, are most likely to be added to the flowsheet in the future.

The following aspects of technology should be considered when selecting additional operations for the flowsheet:

- Integration (in the flowsheet, ease of integration if not in the flowsheet, impact on the balance of the process, complexity)
- Performance (capability to satisfy environmental, safety and mission requirements; significant improvement over baseline)
- Maturity (extent of previous testing, in use commercially, used elsewhere in waste treatment, known problems)

Applicability (waste-specific or all-purpose, baseline or primary technology vs. enhancements, backups or alternatives)

Cost (potential for improved cost profile or life-cycle cost)

Schedule (need dates vs. potential delays)

Stakeholder acceptance (customer and public, improves credibility, consistent with the mission and legal commitments)

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APPENDIX A -- TWRS FLOWSHEET ASSUMPTIONS

This APPENDIX is extracted verbatim (except where explanatory notes are provided within square brackets [...]) from the TWRS Process Flowsheet Revision 1 Section 3.2 TECHNICAL BASES AND ASSUMPTIONS to provide easy access to the technical bases for calculating the mass balance.

[Note: References to APPENDIX A in the following text refer to APPENDIX A in the TWRS Process Flowsheet Revision 1. The tank-by-tank inventory is provided there, not in this document].

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3.2 TECHNICAL BASES AND ASSUMPTIONS

3.2.1 Characterization

3.2.1.1 Tank-by-Tank Inventory Tables

The TWRS Process Modeling group has developed and maintains a master tank-by-tank inventory in an electronic spreadsheet for use in the ASPEN flowsheet model calculations and other studies. The inventory is split into a water soluble fraction and an insoluble fraction on a tank-by-tank basis; an abbreviated tank-by-tank inventory is provided in APPENDIX A [of the TWRS Process Flowsheet]. These tables are derived from the master spreadsheet (fewer components are listed in APPENDIX A to facilitate printing). The components not listed in APPENDIX A are insignificant in terms of mass.

The inventory for DST waste was derived by reviewing primary source documents (Shelton 1994a; Shelton 1995a, Boomer et. al. 1993) as described in APPENDIX A.

The inventory for SST waste was distributed to tanks consistent with the Tank Layer Model (TLM) (Agnew et. al. 1995), then adjusted on a component-by-component basis to be consistent with the totals in the Hanford EIS (DOE 1987). The TLM does not require a charge balance, so in some cases Na or OH⁻ was added to the inventory to achieve a charge balance.

In general, the water soluble fraction is composed of the salt cake predicted by the TLM (assumed to be water soluble) and the water soluble fraction of the sludge. The water soluble fraction of the sludge is determined by periodic sludge washing chemistry evaluations (Colton 1995, Colton et. al 1995) of the available tank characterization reports and washing data for SST sludges. Engineering judgement is required to estimate the water solubility of tank waste. Currently available data is insufficient to develop true tank-by-tank water solubility factors.

Table A-1 in APPENDIX A [of the TWRS Process Flowsheet] lists the mass of water soluble (including retrieval water) and insoluble components in SSTs. Table A-2 is an equivalent table for DST waste. Tanks are listed in the table according to SOWRT group (Hill 1995), which is a model that sorts tanks into groups according to the primary and secondary origin of the waste. Figure 3-1 illustrates that SOWRT groups are unequal in terms of their contribution to the composite feed stream. Figure 3-2 also shows that key insoluble components (non-cancrinitic aluminum and chromium) are confined to a few SOWRT groups. The insoluble phosphate is more widely distributed among the groups.¹²

¹² Distribution of waste into SOWRT groups is presented here for information only. SOWRT groups have no significance in the context of this flowsheet because the feed stream is a composite of all waste. The grouping of waste becomes a factor only when devising operating scenarios.

Figure 3-1 Distribution of Tank Waste By SOWRT Group

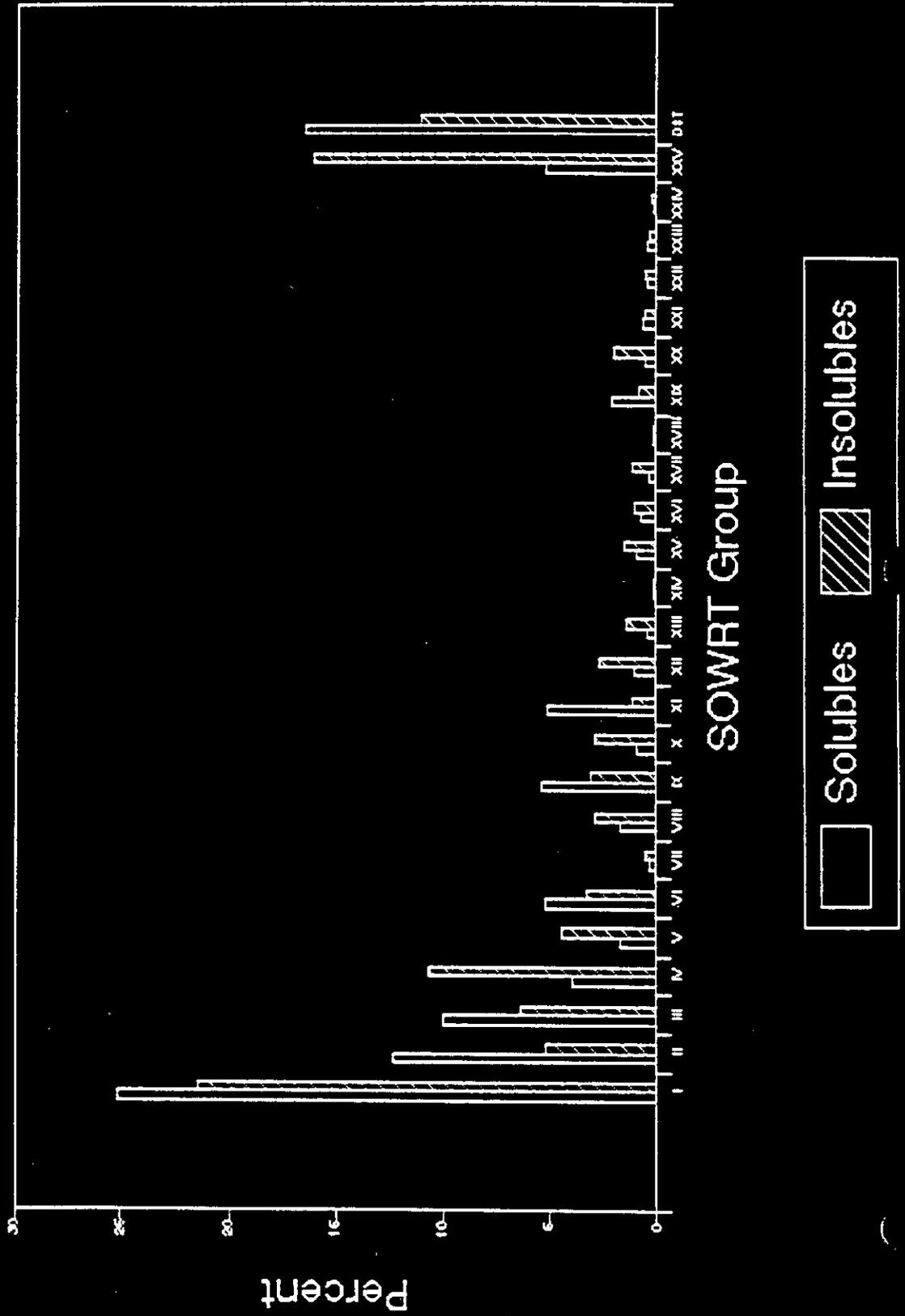
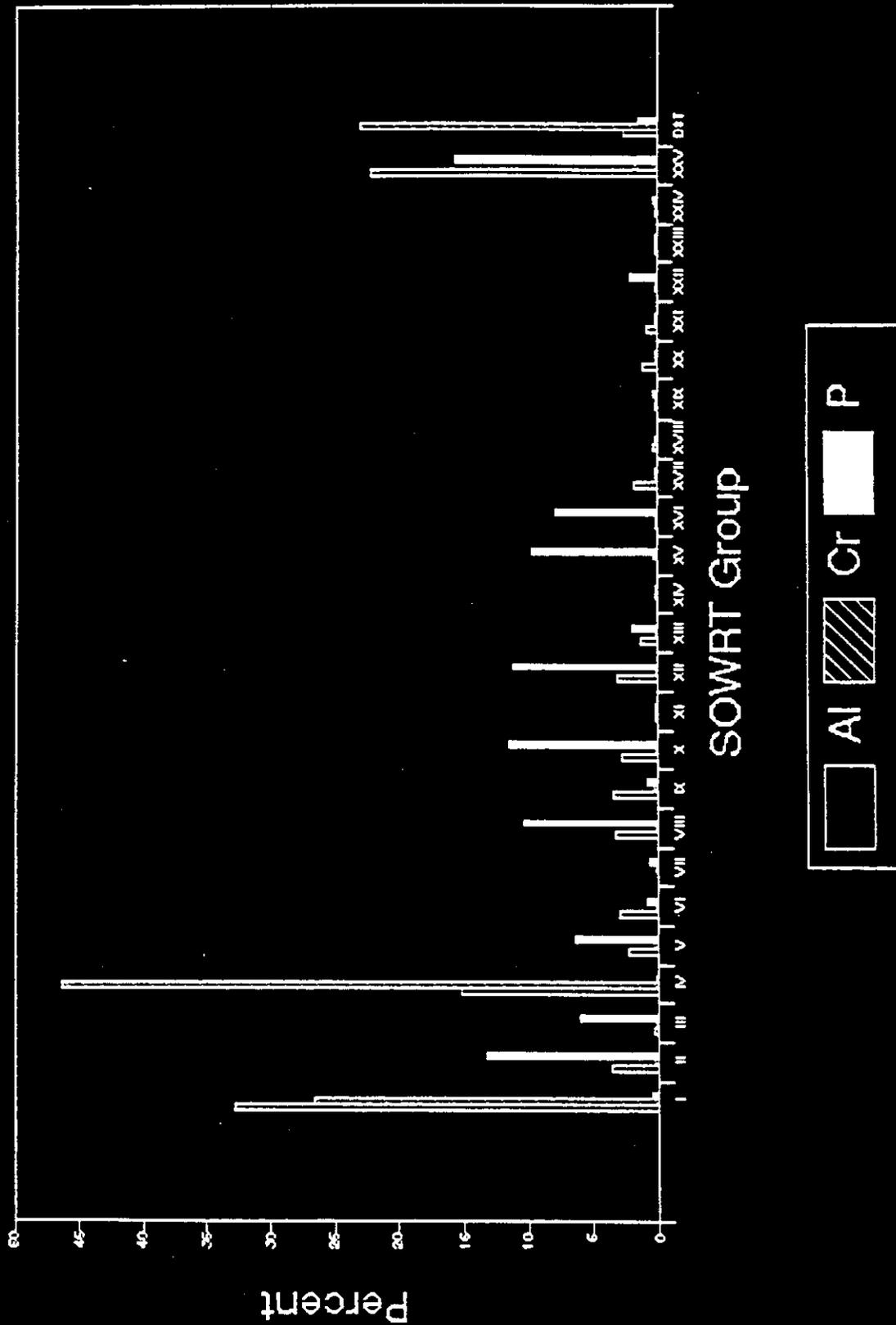


Figure 3-2 Distribution of Tank Waste By SOWRT Group



When Si and Al are present in an SST, a stoichiometric amount of Al is mineralized as $2(\text{NaAlSiO}_4) \cdot 0.52(\text{NaNO}_3) \cdot 0.68(\text{H}_2\text{O})$ (cancrinite). None of the components in cancrinite are susceptible to washing or caustic leaching. Caustic leaching data has shown that Si in sludges can be solubilized to some extent, so this is a conservative assumption.

The development of the tank-by-tank inventory is discussed in detail in APPENDIX A [of the TWRS Process Flowsheet].

3.2.1.2 Overall Inventory

A "short list" of the overall SST and DST tank chemical inventory, derived from APPENDIX A, is shown in Table 3-1. The amount of water reported in Table 3-1 includes the water added for retrieval. Table 3-1 shows the split between soluble and insoluble components after retrieval. (The split between soluble and insoluble varies considerably from tank to tank. This table is an overall composite.)

Table 3-1 Double Shell and Single Shell Tank Inventory

Component	SOLUBLE			INSOLUBLE		
	TOTAL (kg)	SST (kg)	DST (kg)	TOTAL (kg)	SST (kg)	DST (kg)
Total Mass Flow	7.26E+08	5.74E+08	1.52E+08	1.97E+07	1.68E+07	2.88E+06
Al(OH) ₄ ⁻	6.99E+06	2.07E+06	4.93E+06			
Al ⁺³				2.31E+06	2.20E+06	1.11E+05
Bi ⁺³	1.18E+04	9.58E+03	2.23E+03	2.52E+05	2.52E+05	
Ca ⁺²	1.65E+04	6.42E+03	1.01E+04	1.45E+05	1.22E+05	2.28E+04
Cancrinite				2.70E+06	2.70E+06	
Ce ⁺³	2.36E+03	2.34E+03	2.26E+01	2.35E+05	2.32E+05	2.78E+03
Cl ⁻	6.78E+05	4.07E+05	2.71E+05	9.00E+03	7.63E+03	1.37E+03
CO ₃ ⁻²	3.10E+06	1.58E+06	1.53E+06	1.09E+05	3.86E+04	7.04E+04
Cr(OH) ₄ ⁻	4.46E+05	3.13E+05	1.33E+05			
Cr ⁺³				1.60E+05	1.21E+05	3.87E+04
Cs ⁺	1.88E+03	5.16E+02	1.37E+03	2.06E+02	1.76E+02	3.05E+01
F ⁻	1.14E+06	7.80E+05	3.57E+05	6.82E+04	2.62E+04	4.20E+04
Fe ⁺³	3.44E+04	2.37E+04	1.07E+04	7.62E+05	6.07E+05	1.56E+05
H ₂ O	5.08E+08	3.99E+08	1.09E+08			
La ⁺³	2.39E+02	1.88E+01	2.20E+02	2.30E+04	1.86E+03	2.11E+04
Mn ⁺⁴	1.08E+04	2.42E+03	8.39E+03	1.80E+05	1.18E+05	6.15E+04
Na ⁺	6.80E+07	5.34E+07	1.46E+07	7.77E+05	5.42E+05	2.35E+05
Ni ⁺³	8.21E+03	4.07E+03	4.14E+03	2.06E+05	1.99E+05	6.87E+03
NO ₂ ⁻	9.47E+06	4.98E+06	4.49E+06	6.18E+04	5.34E+04	8.40E+03
NO ₃ ⁻	1.07E+08	9.66E+07	9.90E+06	9.85E+05	9.42E+05	4.31E+04
OH ⁻	1.43E+07	9.25E+06	5.08E+06	5.63E+06	4.54E+06	1.09E+06
PO ₄ ⁻³	3.20E+06	2.80E+06	3.93E+05	1.85E+06	1.83E+06	2.15E+04
Si ⁺⁴	1.59E+04	4.06E+02	1.55E+04	2.32E+05	1.41E+04	2.18E+05
SO ₄ ⁻²	2.02E+06	1.63E+06	3.91E+05	2.56E+04	2.19E+04	3.65E+03
Sr ⁺²	3.80E+02	3.62E+02	1.86E+01	3.66E+04	3.60E+04	6.00E+02
TcO ₄ ⁻	2.21E+03	2.00E+02	2.01E+03	9.07E+02	8.65E+02	4.20E+01
TOC	1.06E+06	2.26E+05	8.31E+05	8.73E+04	1.51E+04	7.22E+04
UO ₂ ⁺²	1.06E+05	9.67E+04	9.27E+03	1.54E+06	1.50E+06	3.36E+04
ZrO ₂ ·2H ₂ O	7.53E+03	6.68E+03	8.56E+02	1.20E+06	6.61E+05	5.34E+05

The inventory of radionuclides is taken from the Integrated Data Base (IDB) with some adjustments (Shelton 1995b). The "short list" overall radionuclide inventory is shown in Table 3-2. For detailed listings, see Table A-3 for SSTs and Table A-4 for DSTs [in the TWRS Process Flowsheet].

Table 3-2 Radionuclide Inventory for Single-Shell and Double-Shell Tanks^{1,2,3}

Radionuclides	SOLUBLE			INSOLUBLE		
	TOTAL (Ci)	SST (Ci)	DST (Ci)	TOTAL (Ci)	SST (Ci)	DST (Ci)
Total Activity	6.60E+07	1.48E+07	5.12E+07	1.09E+08	8.62E+07	2.33E+07
Am-241	7.96E+03	2.65E+03	5.31E+03	9.66E+04	2.43E+04	7.23E+04
C-14	3.33E+03	2.98E+03	3.46E+02	2.02E+03	3.01E+01	1.99E+03
Cs-137	3.19E+07	7.18E+06	2.47E+07	3.01E+06	2.29E+06	7.16E+05
Ba-137	3.03E+07	6.82E+06	2.35E+07	2.86E+06	2.18E+06	6.80E+05
Cm-244	1.20E+00	1.20E+00		1.19E+02	1.19E+02	
Np-237	6.95E+00	6.95E+00		6.25E+01	6.25E+01	
Pu-238	3.18E+02	2.17E+01	2.96E+02	2.34E+03	1.07E+03	1.27E+03
Pu-239	1.65E+03	3.44E+02	1.31E+03	2.48E+04	1.69E+04	7.89E+03
Pu-240	4.31E+02	9.15E+01	3.39E+02	6.28E+03	4.18E+03	2.10E+03
Pu-241	4.79E+03	2.29E+03	2.50E+03	7.02E+04	3.36E+04	3.66E+04
Sr-90	1.88E+06	4.12E+05	1.47E+06	5.17E+07	4.08E+07	1.09E+07
Y-90	1.88E+06	4.12E+05	1.46E+06	5.17E+07	4.08E+07	1.09E+07
Tc-99	2.28E+04	8.89E+03	1.39E+04	9.29E+03	8.89E+03	4.04E+02

¹Radionuclides decayed to 12/31/99.
²Amounts are consistent with the 1995 Integrated Database.
³SST is from TRAC; DST is from tank analysis.

3.2.2 Retrieve Waste

The maximum duration of SST retrieval is established in the language of the Tri-Party Agreement. All SST retrieval is completed by September 2018.

Assumption of a steady mass flow of soluble sodium from retrieval to pretreatment suggests a nominal, time-averaged throughput for pretreatment and vitrification, not to be confused with design basis rates for equipment design.

The tank-by-tank inventory provides the flexibility to model the processing of different combinations of tanks. In addition to the "superblend" results, Revision 1 [of the TWRS Process Flowsheet] provides flowsheet results for selected "miniblends" in the appendices.

The actual operation of the retrieval system is outside the scope of the TWRS Process Flowsheet, i.e., retrieval does not appear on the Process Flow Diagrams (PFD).¹³ Some additional information about retrieval parameters is provided in APPENDIX B [of the TWRS Process Flowsheet].

Table 3-3 Primary Retrieval Assumptions

The water soluble fraction of each tank is assumed to be in solution after retrieval water is added.

Retrieval water is added on a tank-by-tank basis to yield a slurry of 5M Na or 10 wt% solids on, whichever amount is larger.

The tank-by-tank inventory is composited to form the feed stream to pretreatment (i.e., the feed stream is a "superblend").

Conditioning of the waste to facilitate long distance transfers occurs in the Retrieval Annexes. Conditioning may include further dissolution of salts, dilution, particle size adjustment and blending. Particles should be no larger than 2 mm to be suspended at normal transport velocity.

No additional DSTs are going to be provided, so in-process storage of SST waste in DSTs is of short duration (no more than 6 months).

¹³ In an operating scenario that considers the implementation of individual retrieval projects, the SST retrieval rates are low for the first few years of operations, and DST solutions are retrieved to keep pretreatment operating at or near full capacity. Pretreatment capacity is phased in: 1/3 of full capacity the first year, 2/3 of full capacity the second year, and full capacity starting in the third year. After the DST inventory has been worked off, an objective of SST retrieval is to keep a relatively constant flow of Na feeding to the pretreatment facility so that pretreatment can continue to operate at or near capacity.

The TWRS Process Flowsheet does not address perturbations to the nominal processing rate that could result from implementation of a specific retrieval plan. The evaluation of retrieval schedules (Certa 1995b), a task that was initiated during FY-1995, is conducted independently of the TWRS Process Flowsheet.

3.2.3 Transfer Waste

Slurry transfer in pipelines is the assumed method of waste transfer. Slurries of small particles (less than 40 microns) behave as non-Newtonian fluids (Perry 1973). The rheology of small particle slurries can be highly dependent on the nature of the particles; for example, boehmite slurries are considerably more viscous than gibbsite at low shear rates. Pipeline design must take the nature of the solids into account.

If larger particles are being transferred, the transfer system must also be capable of maintaining the minimum transport velocity. Minimum transport velocities are normally correlated using solids concentration, relative densities, particle diameter, and pipe diameter (Durand 1953, Hughmark 1961, Spells 1955). Pipeline design should consider up to 10 wt% slurry at a liquid specific gravity of 1.0 to 1.25, which corresponds to a carrier liquid ranging from very dilute to 5M NaNO₃ solution.

3.2.4 Store In-Process Waste

Waste retrieved in the West Area is accumulated in the SY tank farm and transferred to the AN tank farm. Waste retrieved in the East Area is accumulated in the AN tank farm. The AN tank farm feeds the TWRS treatment complex. Pretreated solids are transferred from the treatment complex via the AN tank farm to interim storage in aging waste tanks and the AW tank farm. Cesium concentrate is stored in an aging waste tank.

In-process waste storage requirements are driven by a number of factors: successfully matching retrieval rates and pretreatment, facility configuration decisions, and the extent to which the process areas are close coupled (or the desire to decouple process areas from each other). The close coupled facility approach in this flowsheet represents the minimum storage requirement for liquids.

3.2.5 Pretreat Waste

To minimize in-process storage requirements for the large volume of retrieved liquids, the pretreatment processing capacity should be based on a 14 year duration (assuming that full capacity is not achieved until the third year, the actual duration of processing is 15 years) to coincide with the 14 year duration of retrieval.

Revision 1 provides no special treatment for the small volume of TRU/Sr contaminated liquids in the inventory. Adjustment of the hydroxide concentration, chemical displacement with cations (iron, strontium), chemical oxidation and heat treatment are under consideration for the in-tank treatment of these special wastes. The exact conditions for treatment will be defined in a future revision of the flowsheet, if required. These are non-reference separations at this point in time and do not appear in the flowsheet. In-tank separations processes were recently documented (Schulz et. al. 1995).

3.2.5.1 In-Tank Enhanced Sludge Washing

In-tank enhanced sludge washing includes a retrieval wash (i.e., the solubilization of some components that actually occurs during retrieval and transfer of the slurries), solid/liquid separations by settle/decant, caustic leaching of selected components (Al, PO_4^{3-} , Cr and Na are the primary targets of leaching) from the solids, and washing of the leached solids with dilute caustic.

The split between liquid phase and solid phase in the retrieval wash is discussed in Section 3.2.1. The split is built into the inventory tables.

Table 3-4 shows a summary of experimental washing and caustic leaching results that were available as of this writing (Lumetta et. al. 1993, Rapko et. al. 1995, Temer et. al. 1995). The leach efficiencies applied to the inventory of each type of SST waste yields a mass-weighted efficiency for caustic leaching.

The Al leach efficiency deserves additional explanation. During the experimental procedure, S-104 and U-110 samples (high aluminum content sludges) were treated with caustic at 100 °C and allowed to cool to near ambient temperature before analyzing the Al. Felmy's evaluation (not yet published) of these experiments in Figures 3-3 and 3-4 shows that the experimental Al concentration in room temperature samples of caustic leach solution was at the solubility limit, meaning that revised experimental conditions could very likely improve the efficiency of Al leaching. Assuming 62% for caustic leaching of boiled REDOX wastes in place of the experimental 35%, the overall SST leach efficiency for Al in this flowsheet is 67% instead of 55%.

The Cr and PO_4 leach efficiencies are unchanged from the laboratory values. Therefore, the SST caustic leach efficiency derived from Table 3-4 for Al, Cr, and PO_4 is 67%, 60%, and 74%, respectively.

Revision 0 of the flowsheet took no credit for Na leaching. The mass weighted average for the Na_2O content in the leached sludges of 9 recent core samples¹⁴ (B-111, B202, BX-105, BX-107, C-103, C-108, S-104, T-107) is 11%. To obtain a residual sludge composition of 11% Na_2O for the TWRS composite feed, a 25% caustic leach efficiency is required. Therefore, a 25% caustic leaching efficiency for Na is applied to both SSTs and DSTs.

The caustic leach efficiencies for DSTs is assumed to be the same as the previous basis of 85%, 75%, and 70% for Al, Cr, and PO_4 , respectively.

Together, the assumptions for SSTs and DSTs discussed above result in overall caustic leach efficiencies of 68%, 64%, 74%, and 25% for Al, Cr, PO_4 , and Na, respectively.

¹⁴The T-104 data point was eliminated as a statistical outlier.

The TRU content (both soluble and insoluble) of the combined supernatants (waste liquor, leachates and wash water) resulting from the in-tank enhanced sludge washing process should average <100 nCi/g and <540 nCi/g of sodium. This will ensure that the final LLW product is <100 nCi of soluble TRU/g of LLW glass, assuming all TRU in the supernatants goes to LLW glass.

The remainder of the assumptions pertaining to enhanced sludge washing are summarized in Table 3-5.

Table 3-4 Mass Weighted Wash and Leach Efficiency for SSTs

Waste Type	Aluminum			Chromium			Phosphate		
	Wash (% of Total Al)	Leach 1 (% of Total Al)	Leach* 2 (% of H ₂ O Insoluble Al)	Wash (% of Total Cr)	Leach 1 (% of Total Cr)	Leach* 2 (% of H ₂ O Insoluble Cr)	Wash (% of Total P)	Leach 1 (% of Total P)	Leach* 2 (% of H ₂ O Insoluble P)
BiPO ₄	7	54	58	16	40	47	72	26	94
TBP	2	79	81	37	51	82	22	36	46
REDOX	22	60	77	80	19	95	99	0	0
REDOX ^b (boiled)	4	34	35/62	45	52	95	9	0	0
PUREX	51	21	43	4	7	7	70	0	0
SST Mass-Weighted Average	17	46	55/67	55	27	60	64	26	74

^aLeach 2 = (Leach 1)/(1-Wash/100)

^bThe Al leach efficiency for boiled REDOX waste was adjusted as explained in the text. The overall efficiency changed from 55 percent to 67 percent as a result of the adjustment.

BiPO₄ bismuth phosphate wastes
 TBP tri-butyl phosphate wastes
 REDOX reduction oxidation (S Plant) wastes
 PUREX plutonium-uranium extraction wastes

Figure 3-3. Experimental and Calculated Aluminum Solubilities (S-104).

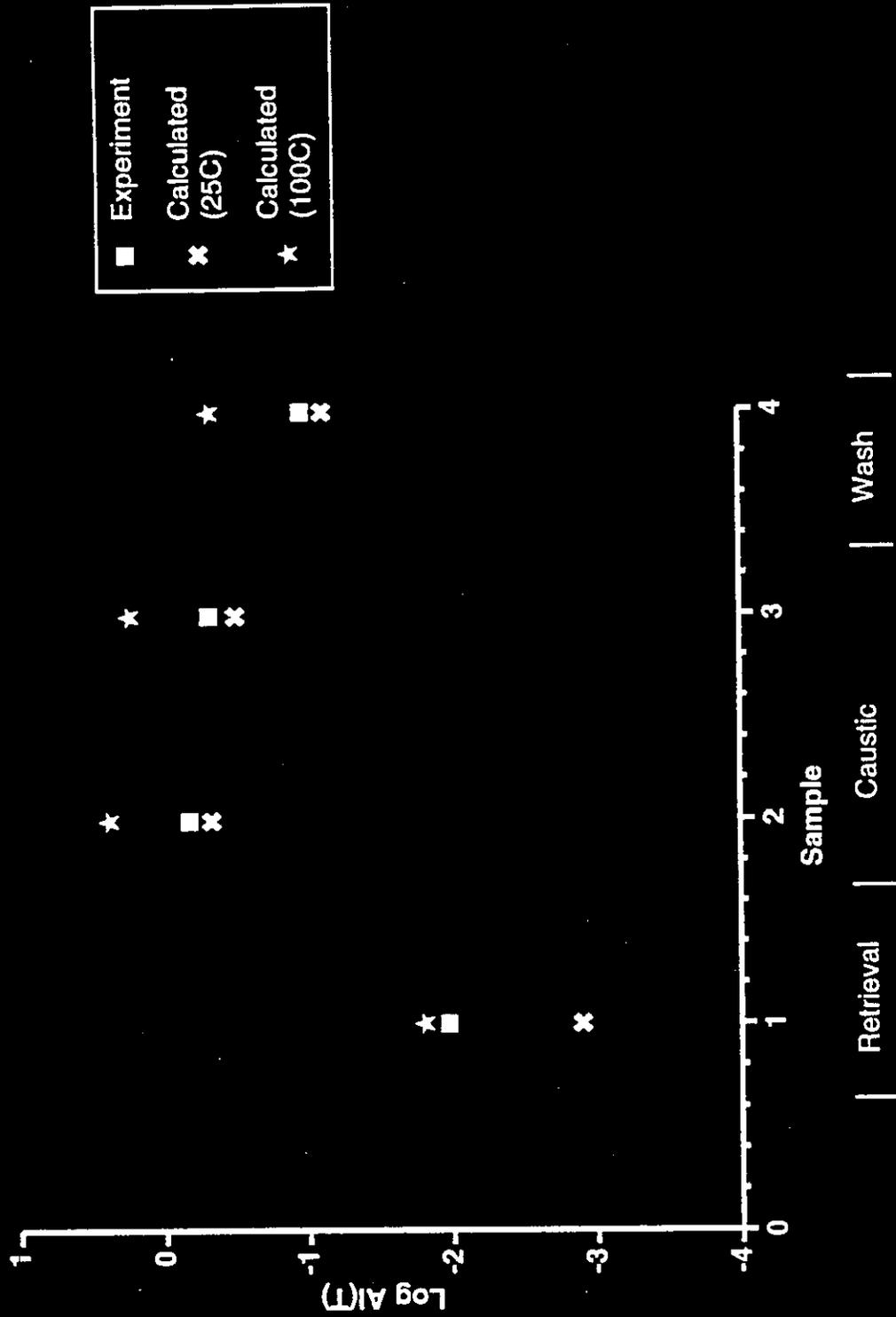


Figure 3-4. Experimental and Calculated Aluminum Solubilities (U-110).

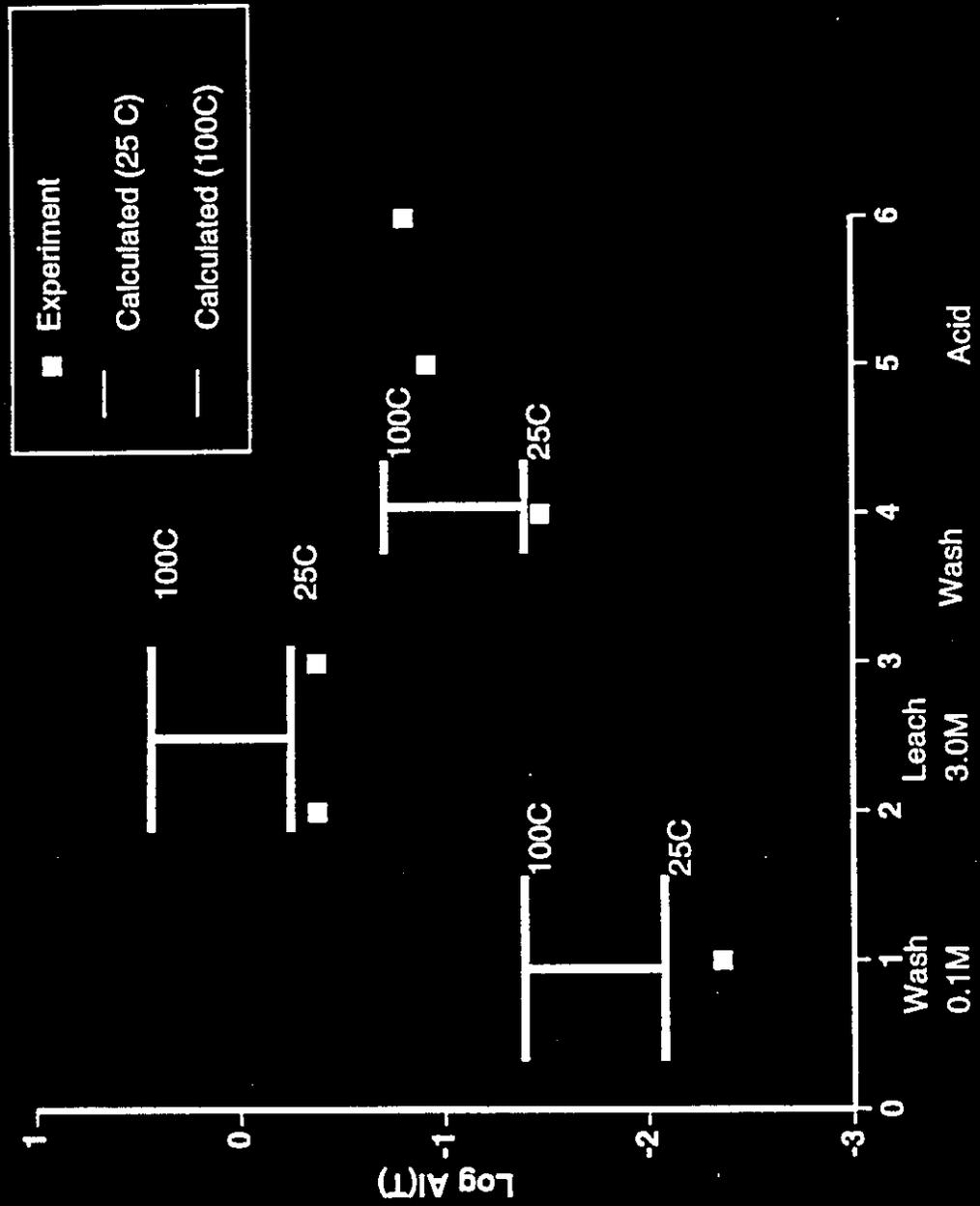


Table 3-5 Primary Assumptions for Enhanced Sludge Washing

Flocculent Additions: Polyelectrolyte with 4 H to 1 C (this is just a placeholder until the flocculent is actually selected). Flocculent is prepared as a 10 wt% solution. Flocculent is added to slurries at 0.019 kg of flocculent per kg of dry solid. Settled solids tie up 80% of the flocculent.

1st Stage Settling: Decanted liquids entrain 0.33% of incoming solids. Settled sludge is 20 wt% solids. Al, Cr, phosphate and Na leach from solids with efficiencies of 68%, 64%, 74% and 25%, respectively. Moles of OH⁻ consumed by leaching is 1 mole/mole Al, 1 mole/mole Cr, 3 moles/mole of phosphate. Chemical addition results in an 8 wt% slurry (Stream 14) with 3M free OH⁻ and 0.01M NO₂ after leaching has gone to completion.

No further solubilization occurs after the caustic leach. Washing of the leached solids is modelled as simple dilution of the interstitial liquor.

First Wash Tank: Decanted liquids entrain 0.33% of incoming leached solids. Settled sludge is 20 wt% solids. Chemical addition results in an 8 wt% slurry (Stream 21) with 0.1M free OH⁻ and 0.01M NO₂. This addition is the first wash.

Second Wash Tank: Same as First Wash Tank (except Stream 21 is Stream 28).

Third Wash Tank: Same as First Wash Tank (except Stream 21 is Stream 51).

Fourth Wash Tank: Decanted liquids entrain no solids. Otherwise same as First Wash Tank (except Stream 21 is Stream 58).

2nd Stage Settling: Same as 1st Stage Settling.

Aqueous makeup provides 50 wt% NaOH and 50 wt% NaNO₂ for chemical additions.

The long range goal in this series of flowsheet revisions is to account for waste solubility and leach efficiency on a tank-by-tank basis using Tank Layer Model distributions, the results of sludge experiments, and the results of chemical modelling. Until the body of laboratory data is complete enough to do true tank-by-tank calculations, mass weighted averaging of the available data supplemented by engineering judgement is the next best alternative.

3.2.5.2 Evaporation

The process has the capability to condition combined filtrates by evaporation, chemical adjustment, and polishing filtration in preparation for ion exchange. Ion exchange feeds that have been concentrated can be treated more efficiently than a dilute feed (Kurath et. al. 1994).

Table 3-6 Primary Assumptions for Evaporator and Condenser

<p>Filtrate is evaporated to 7M Na for equipment design basis.¹⁵</p> <p>Solids formed in the evaporator are removed by downstream polishing filter.</p> <p>Condenser recovers 99% of water vapor.</p> <p>Distribution coefficient (Bottoms/Condensate): 5E+6 for Cl and NO₃, 3.5E+5 for TOC, and 1E+7 for everything else (Na in condensate is adjusted to maintain the charge balance).</p> <p>Bottoms are not returned to DSTs, although a routing is provided.</p>

3.2.5.3 Polishing Filtration

Evaporator bottoms are filtered through a deep bed frit filter to prevent blinding in the ion exchange columns. When spent, the filter bed is flushed out and combined with the Cs-depleted ion exchange effluent in the LLW evaporator feed tank.

Table 3-7 Polishing Filter Assumptions

<p>Frit composition: 77% SiO₂, 15% B₂O₃, 6% Li₂O, 1% CaO, 1% MgO</p> <p>Frit replacement: 45 kgs (100 lbs) every 3.785E+5 L (100,000 gal)</p> <p>Filter efficiency: 1% of solids pass through the filter</p> <p>Filter flush: 2 wt% solids in the flush slurry</p>

3.2.5.4 Ion Exchange

Analysis of experimental data and engineering assessments conducted during 1994 have provided an improved technical basis for modelling the ion exchange removal of Cs (Kurath et. al. 1994; Eager 1994; Johnson 1995). An empirical correlation to predict the cesium distribution (lambda value) of the baseline resin over a range of concentration and temperature is now available. The lambda value and a semi-empirical column breakthrough equation are used

¹⁵ Filtrates should be concentrated to the extent permitted by their chemistry. A short evaporation study (Powell 1995) determined that evaporation to 7M Na is about the onset of precipitation in a variety of wastes; the chemistry of other waste may limit the extent of evaporation.

for calculating cumulative Cs losses (i.e, bed volumes to breakthrough). The lambda correlation and the breakthrough calculation are discussed in more detail in Section 5.0. On the average, 35 bed volumes are treated between elutions, ranging from 8 to 43 bed volumes depending on the type of feed.

For Revision 1, Na and K are assumed to load on the bed in the same ratio that exists in the feed. Insufficient data is available at this point in time to define the loading behavior of other cations. Ca, Sr, Pu and Am, for example, are expected to load to some extent, but their behavior has not been tracked in column loading studies. This area needs to be addressed in future loading studies.

The column configuration is a notable change in Revision 1. There are redundant ion exchange lines, each consisting of two columns in series. From a design standpoint, this change substantially reduces pipe and valving complexity.

The parameters selected for modelling ion exchange are as follows:

Table 3-8 Assumptions for Ion Exchange Modelling

Parameter	Value
Number of Beds in Series	2
Volume of Bed	6500 L
Volume of Series	13000 L
Feed Flowrate	1 BV/hr
Number of BVs Before Regeneration ¹	Calculated from correlations Cum. Cs loss = 1 Ci/5000 moles Na
Cesium Elution	
Residual Feed Flush	2 BV Water at 2 BV/hr
Sodium Scrub ²	
Cesium Elution	6 BV 0.5M HNO ₃ at 1 BV/hr
Residual Eluent Flush	2 BV Water at 2 BV/hr
Bed Regeneration	1 BV 0.5M NaOH at 2 BV/hr 1 BV 2.0M NaOH at 2 BV/hr

¹ Resin degrades to 80% of its original capacity after 10 cycles. To account for degradation of resin capacity with time, the model regenerates the bed at 90% of the calculated number of bed volumes.

² The sodium elution step (sodium scrub) that preceded cesium elution in Revision 0 has been omitted in Revision 1. The primary benefit of the sodium scrub was to reduce the amount of sodium in the Cs eluate, the down side being increased cycle time and Cs losses to the LLW. In the current flowsheet, the Cs eluate is neutralized and returned to the DSTs prior to vitrification. The value of a sodium scrub has not been determined for these conditions. A sensitivity study may be justified to evaluate the pros and cons of a sodium scrub.

Cumulative loss of 1 Ci/m³ in 5M Na liquid effluent is a technically feasible target, thus satisfying the NRC "incidental waste" requirement (See Section 5.1.3). The total amount of cesium to near surface disposal is considerably less than the amount that has been accepted by the NRC in past

negotiations. Cumulative loss is a more meaningful measure of cesium removal efficiency than percent removal (or DF) since it is consistent with the non-steady state nature of the ion exchange operation, and also reflects in unambiguous terms the curies of Cs that are permitted to break through to LLW.

The cesium removal process is based on the cation exchange resin CS-100 manufactured by Rohm and Haas. Although it is not the highest capacity resin for Cs, CS-100 has produced the most consistent results under simulated waste processing conditions of the commercially available resins tested. The cesium will be loaded on the resin at high alkaline conditions ($\text{pH} \geq 12$) from clarified supernatant at about 25 °C.

After 10 cycles (nominally 350 bed volumes) the cesium capacity of the resin has degraded to 80% of the fresh resin capacity. Spent resin will be flushed into the ion exchange effluent stream and fed to the LLW melter.

3.2.5.5 Eluate Treatment

The eluate stream, which is mostly nitric acid and water, with some sodium nitrate and a little cesium nitrate, is evaporated and neutralized with caustic to a free hydroxide concentration of 0.1M.

Table 3-9 Eluate Treatment Assumptions

<p>Evaporate 90% of the water and 70% of the nitric acid.</p> <p>Condense 99% of the vapor and recycle for elution.</p> <p>Neutralize bottoms to 0.1M OH⁻.</p>

3.2.6 Immobilize Low-Level Waste

3.2.6.1 LLW Feed Evaporator

Table 3-10 Primary Assumptions for Evaporator

<p>Feed is evaporated to 10M Na for equipment design basis.</p> <p>Ignore solids (salts) formed in the evaporator.</p> <p>Distribution coefficient: same as filtrate evaporator.</p> <p>Bottoms are not returned to DSTs, although routing is provided.</p>

3.2.6.2 LLW Glass Formulation

Time-phased process modelling shows that a more uniform glass results over time if sodium is held constant (Orme 1995). When NaOH is added to high Al waste feeds to hold Na₂O at 25 wt%, the variation in SiO₂ dampened considerably.

Chemical additions to the LLW melter are made to bring the melt within the formulation constraints stated in Table 3-11, while minimizing the amount of glass. The possible additives are SiO₂, Al₂O₃, and CaO.

Typical composition ranges for soda-lime-boro-alumina-silicate systems are 15 to 25 wt% Na₂O, 0 to 12 wt% CaO, 0 to 12 wt% B₂O₃, 5 to 12 wt% Al₂O₃, and 40 to 60% SiO₂ (Wilson et. al. 1995). The glass formulation constraints are consistent with the low end of glass production capacity; the loading for sodium, in particular, needs to be verified by demonstration.

Table 3-11 LLW Glass Formulation Constraints

Na ₂ O	= 25 wt%
Na ₂ O + K ₂ O	<= 30 wt%
Al ₂ O ₃	= 5 wt%
CaO	= 10 wt%
SiO ₂	>= 50 wt%

3.2.6.3 Melter Energy

Energy in the melter is provided by combustion. The minimum energy requirement is based on the vaporization and super heating of water to 1200 °C and the melting of the major constituent oxides. The model uses 2% more energy (i.e., kerosene) than the minimum. The heat of melting for the following oxides is considered:

Table 3-12 Heat of Melting

Na ₂ O	11.4 kcal/gmole
Al ₂ O ₃	28.0
CaO	19.0
SiO ₂	2.3
B ₂ O ₃	5.8
Li ₂ O	14
MgO	18.5

Kerosene has a heat of combustion of 11,111 kcal/kg. The kerosene assay is 87.3% C, 12.6% H, 0.04% O, and 0.06% N. Oxygen for combustion is added in 10% excess.

3.2.6.4 Volatility From LLW Combustion Melter

The fractional volatility of the melt is as shown in Table 3-13. In addition to volatility, there is physical entrainment of 2% of the glass (Boltdt 1995). The composition of entrained glass is determined after volatilization.

Table 3-13 LLW Melter Volatility Assumptions

Component	% Volatile	Comment
B ₂ O ₃	25	as NaBO ₂
CdO	33	as Cd(OH) ₂
Cl	95	as HCl
Cs ₂ O	33	as CsOH
F	67	as HF
I	100	as HI
K ₂ O	(K/Na ratio same as feed)	as KOH
MoO ₃	5	as Mo(OH) ₆
Na ₂ O	1	as NaOH
NO _x	6,000 ppm noncond 20% NO	
PbO ₂	33	as Pb(OH) ₄
PO ₄	20	as H ₃ PO ₄
Ru ₂ O ₃	33	as Ru(OH) ₃
Se ₂ O ₃	33	as Se(OH) ₆
SO ₄	90 10	as SO ₂ as SO ₃
Tc ₂ O ₇	50%	as TcO ₂
TeO ₃	33	as Te(OH) ₆

3.2.6.5 LLW Cullet

The glass cullet operation (quench flume, roll crusher, screen, and lag storage) produces a glass "gravel" that is capable of pneumatic transfer. The heat capacity of glass varies greatly over the range 1200 to 100 °C, but assuming an average of 0.36 kcal/kg°C, the following assumptions result in a ~20 °C temperature rise in the recirculating quench water. The heat load on the quench flume condenser depends on the nominal operating temperature of the flume, which has yet to be determined.

Table 3-14 Cullet Assumptions

Quench Flume: Quench water 20 times the amount of glass.
Quench Flume Condenser: Condenses 1% of quench water.
Roll Crusher: Converts 1% of glass cullet to fines.
Quench Water Chiller: Removes heat not removed by flume condenser, and controls the temperature of the recirculating quench water.
Cullet Screen: Screen captures all glass except fines, water wash equal to incoming glass, screened cullet holds up 2% of wash water.
LLW Filter Catch Tank: Quench recycle water 20 times the amount of glass, and 0.1% of the fines. 99.9% of fines recycle to melter.
Cullet Storage: Drying air dewpoint 16 °C. Outlet air dewpoint 30 °C. Remove 99% of water. Bins are sized for 7-day PCT turnaround.
Pneumatic Transport: 7.16 kg air per kg dry glass cullet. Cullet cyclone removes 99.999%. 1% of glass cullet is routed to rework.
Rework: Rework cyclone removes 99.999%. Roll crusher produces pumpable size distribution. Rework slurry is 20 wt% crushed glass.

3.2.6.6 Sulfur Concrete Production

Glass cullet is mixed with sulfur polymer cement and cast in 32 m³ canisters. This canister was developed specifically for immobilizing glass cullet in a sulfur matrix (Mitchell 1995).

Table 3-15 Sulfur Concrete Assumptions

Sulfur polymer cement (SPC) is 95% S, 2.5% DCPD and 2.5% CPD.
SPC and glass cullet are mixed as a 30 vol%/70 vol% mixture.
Containers are transported to vault disposal.

3.2.6.7 LLW Melter Offgas Treatment

LLW melter offgas treatment consists of a quench tower, venturi scrubber, demister, HEPA filtration, SO₂ absorption, and catalytic reduction of NO_x. Quenching is rapid cooling and condensing of a gas/vapor stream with a liquid spray. A venturi scrubber completes the particulate removal. Clean air requirements are assumed to drive SO_x and NO_x removal.

Table 3-16 LLW Melter Offgas Treatment Assumptions

<p>Quench Tower: The quench liquid is 1.5M nitric acid. Quench flow rate is 26.54 times the water in melter offgas plus 2 times the gases in melter offgas. The gas effluent from the quench tower is saturated with quench liquid vapor at 75 °C (0.40 lbs vapor per lb of gases) and entrains 7.6 L (2 gal) of quench liquid per 1530 scfm of gas. Removes 100% of TcO₂, 95% of Hg, Cl and other solids.</p>
<p>Venturi/Separator: The scrub liquid is 1.5M nitric acid. Liquid flow to venturi is 1 volume per 1000 volumes of gas. The gas effluent from the venturi/separator is saturated with quench liquid vapor at 75 °C (0.4 lbs vapor per lb of gas) and entrains 7.6 L (2 gal) of quench liquid per 1530 scfm of gas. Removes 95% of Hg, Cl and other solids.</p>
<p>Demister: Removes 95% of Hg, 98% of solids. The gas effluent is saturated at 30 °C (0.0265 lbs vapor per lb of gas), with no entrainment of liquid. Demister wash is set to zero.</p>
<p>Scrub Solution Tank: Maintain at 1.5M nitric acid. TcO₂ converts to TcO₄⁻.</p>
<p>CuO Bed: Removes 90% of SO₂. Maintain 10% excess O₂ in reactor feed. Reactor chemistry is SO₂+O₂+CuO => CuSO₄. Cu/S mole ratio is 2.0 at full loading.</p>
<p>NO_x Reactor: Reduces ~99% of NO_x. Maintain 10% excess NH₃ in reactor feed. Reactor chemistry is NO+0.5O₂ => NO₂ and 3NO₂+4NH₃ => 3.5N₂+6H₂O.</p>

Quench tower flow rate are based on ASPEN simulations. Entrainment assumptions are based on New Waste Calcining Facility design criteria (INEL). Venturi scrubber flow rate based on Perry's Handbook.

3.2.6.8 Chloride Removal From Scrub Solution

Table 3-17 Chloride Removal Assumptions

<p>Acid Evaporator Feed Tank (TK-1100): 25% of the recycled scrubber solution is diverted to chloride removal. No acid added (feed should already be 1.5 M HNO_3).</p>
<p>Acid Evaporator (EV-1102): Condensate carries 83% of water, 25% of HCl, 74% of HF, 18% of HNO_3. Distribution coefficient for everything else is 10^7.</p>
<p>Acid Distillation Column (T-1106): Overheads carry 92% of water, 99.9% of HCl, 99.9% of HF, 0.035% HNO_3. Nothing else in overheads.</p>
<p>Acid Rectifying Column (T-1107): Bottoms carries 10% of water, 87% of HCl, 40% of HF, 92% of HNO_3. Nothing else in bottoms.</p>
<p>HCl Catch Tank (TK-1109): NaOH is added stoichiometrically to neutralize all H^+, $\text{Ca}(\text{OH})_2$ is added at stoichiometric + 10% to precipitate F^-, $\text{Ca}(\text{OH})_2$ is added as a 10 wt% slurry.</p>
<p>Acid Recycle Catch/Neutralization Tank (TK-1110): $\text{Ca}(\text{OH})_2$ is add at stoichiometric + 10% to neutralize H^+, the 10% excess precipitates F^-, $\text{Ca}(\text{OH})_2$ is added as a 10 wt% slurry.</p>
<p>Grout Feed Evaporator (EV-1113): Removes water to make bottoms 5 M Na, "Others" removed like other evaporators.</p>
<p>Condenser (EC-1114): Acts like other condensers.</p>
<p>Grouting Process: Grout chemicals added equal to mass flow of stream 1122, Grout chemicals are 50% Flyash and 50% Cement, All components are solidified.</p>

3.2.6.9 Sulfur Recovery

Sulfur recovery is completed by regenerating the CuO beds to release H_2S , partial burning of the H_2S to SO_2 , and reduction to elemental sulfur in Claus Reactors.

Table 3-18 Sulfur Reduction Assumptions

CuSO₄ Bed: Removes 100% of sulfur. Feed 10% excess H₂ to CuSO₄ bed. Reaction chemistry is $\text{CuSO}_4 + 5\text{H}_2 \Rightarrow \text{H}_2\text{S} + 4\text{H}_2\text{O} + \text{Cu}$. Regenerate CuO bed with air purge.

Combustion Chamber: Add enough fuel to initiate the reaction (1 MT). One-third of H₂S is converted to SO₂. Reaction chemistry is $\text{H}_2\text{S} + 1.5\text{O}_2 \Rightarrow \text{SO}_2 + \text{H}_2\text{O}$.

Claus Reactors: Convert 90% in first reactor. Convert 90% in second reactor. Reactor chemistry is $2\text{H}_2\text{S} + \text{SO}_2 \Rightarrow 3\text{S} + 2\text{H}_2\text{O}$. Gas effluent is recycled to feed SO₂ absorbers.

3.2.7 Immobilize High-Level Waste

3.2.7.1 HLW Melter Feed Preparation

Table 3-19 HLW Melter Feed Preparation Assumptions

Centrifuge: Centrate is 0.1 wt% solids. Liquid carryover in solids is 0.12 times the centrifuged solids.

Centrate Evaporator and Centrate Evaporator Condenser: Evaporate centrate to the extent that Stream 311 is a 20 wt% slurry. Distribution coefficient (Bottoms/Condensate) 5E+6 for Cl and NO₃, 3.5E+5 for TOC, and 1E+7 for everything else (Na in condensate is adjusted to maintain the charge balance)

Feed Adjustment Reactor (FAR): Oxides with lower limits in glass are added to meet the glass composition envelope in Table 3-22, while minimizing the amount of HLW glass produced. Glycolic acid (70.6 wt%) solution added in amount equal to 0.486 of the waste oxides is in excess of the requirement. FAR evaporates water so melter feed contains at least 0.376 kg of oxide equivalent per kg.

FAR Reactions: Carbonate converts to CO₂, 50% of nitrite converts to NO, N₂O, CO₂, and water, 90% of Hg⁺⁺ reduced to Hg by glycolic acid.

FAR Offgas: Contains all gases. Contains 90% of all types of mercury, 98.6% of NH₃, and 0.03% of carbonate, nitrite, nitrate, sulfate, TOC and glycolic acid plus 0.005% of all other components.

FAR Condenser: The FAR offgas passes through the condenser as follows: 100% of all gases, 50% of mercury, and 10% of everything else.

3.2.7.2 HLW Glass Formulation

Working HLW glass limits based on HWVP limits are assumed. The formation of $AlPO_4$ reduces the amount of Al_2O_3 and P_2O_5 present in the glass. Aluminum limit is total Al as Al_2O_3 . Phosphorus limit is total P as PO_4 . All other components are fully oxidized.

Table 3-20 HLW Glass Formulation Constraints

Component	Glass	
	Lower	Upper
Total Al as Al_2O_3	1.0%	11.0
B_2O_3	7.0%	17.0%
CaO		7.0%
Cr_2O_3		0.5%
Fe_2O_3	4.0%	12.0%
Li_2O	2.0%	6.0%
MgO		5.0%
Na_2O	7.0%	12.5%
Total P as PO_4		4.0%
SiO_2	46.0%	56.0%
SO_3		0.5%
ZrO_2		10.0%
Crystallinity Specifications		
$Al_2O_3+ZrO_2$	<=14.0%	
$Al_2O_3+ZrO_2+Fe_2O_3$	<=21.0%	
MgO+CaO	<=8.0%	
$Rh_2O_3+Ru_2O_3$	<=0.25%	

3.2.7.2 Volatility From HLW Melter

Physical conditions and chemistry in the HLW melter are quite different from the LLW melter. Volatilization occurs in the cold cap, but the cold cap also functions as a barrier to physical entrainment. All components except Al and PO_4^- and those noted in Table 3-21 are completely oxidized and remain in the glass. Some gases volatilized from $NO_{x(aq)}$ undergo further gas phase reactions.

Table 3-21 High Level Melter Volatility Assumptions

Component	% Volatile	Comment
B_2O_3	1.0%	
CdO	14%	
Co_2O_3	0.33%	
Cl	0.1% 50% of balance	as Cl_2 as solid Cl
Cs_2O	7.1%	
F	0.1% 25% of balance	as F_2 as solid F
K_2O	0.33%	
MoO_3	1.0%	
Na_2O	0.33%	
NO_x	100%	75% as NO and O_2 92% of remainder as N_2 and O_2 100% of remainder as NH_3 and O_2 ¹
PbO_2	10%	
Ru_2O_3	2.5%	
SeO_3	10%	
TcO_4	50% 7.1%	as TcO_2 as Tc_2O_7
TeO_3	10%	

¹ 20% of NH_3 reduces to NO and H_2O ; 75% of remainder to N_2 and H_2O .

3.2.7.3 HLW Melter Offgas Treatment

Table 3-22 HLW Melter Offgas Treatment Assumptions

Quench Tower: The quench liquid is water. Quench flow rate is 26.54 times the water in the melter offgas plus two times the gases in the melter offgas. The gas effluent is saturated with water at 75 °C (0.40 lbs vapor per lb of gas) and entrains 7.6 L (2 gal) of quench liquid per 1530 scfm of gas. Removes 100% of TcO_2 , 95% of Hg, 95% of water, 95% of all solids. Solubility of NO in quench water is 1%; of SO_2 is 20%. No acid additions to quench water.

Venturi/Separator: Removes 100% of Hg, 95% of water, 50% of NH_3 , 95% of all solids.

Demister: Removes 85% of water, 98% of solids.

Scrub Solution Tank: TcO_2 converts to TcO_4^- .

Mercury Recovery: Knockout chiller removes 90% of Hg from FAR condenser vent.

Ammonia Destruction Tank: Inoperative

Condenser Vent Gas Scrubber: Removes 95% of NH_3 and 90% of Hg and other non-gaseous compounds.

Secondary Waste Evaporator: 100% of spent MOG scrub feeds the evaporator. Boils off 75% of water, 75% of NH_3 , 5 % of NO_3 , NO_2 , SO_3 , CO_3 , and TOC and 0.2% of everything else. No water or chemical additions.

Salt Waste Adjustment Tank: Inoperative. Salt waste recycled to HLW receiving vault (Tk-300 A,B,C,D,E,F).

3.2.7.4 HLW Package

The canister is the TWRS reference canister with a net glass volume of 1.26 m³. The mechanical operations of canister closure, decontamination, smear testing, etc. are not depicted in this flowsheet.

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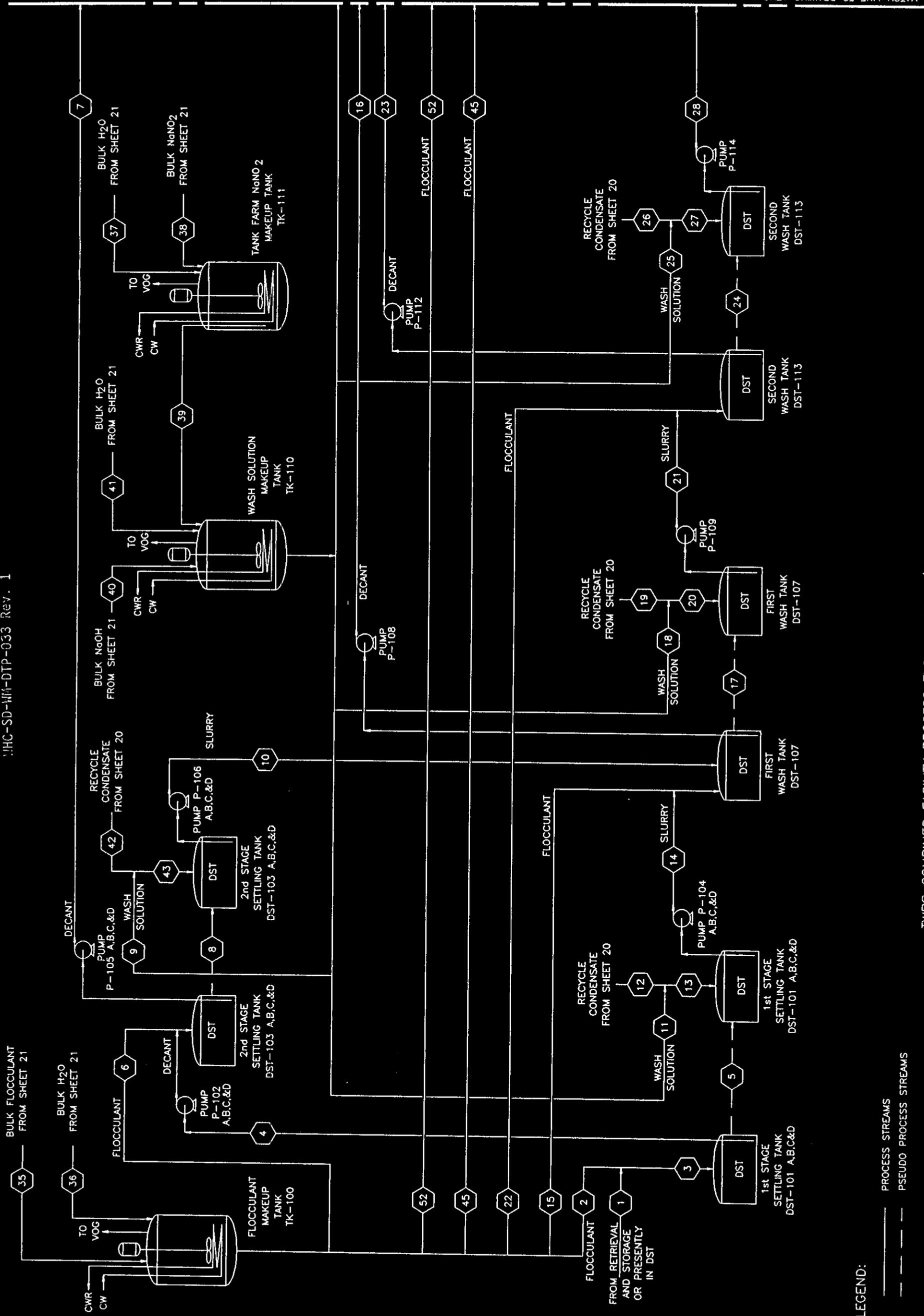
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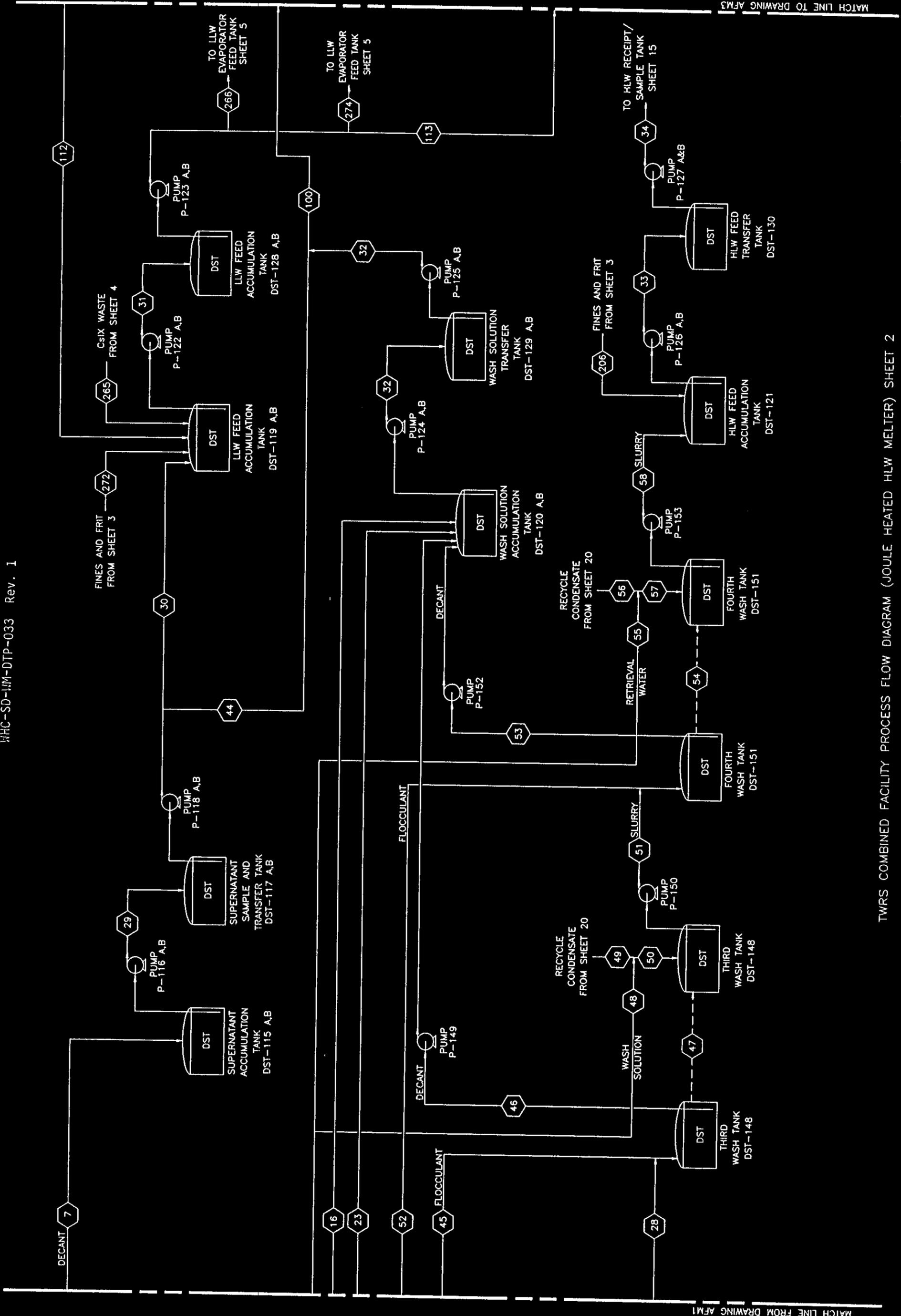
APPENDIX B -- PROCESS FLOW DIAGRAMS

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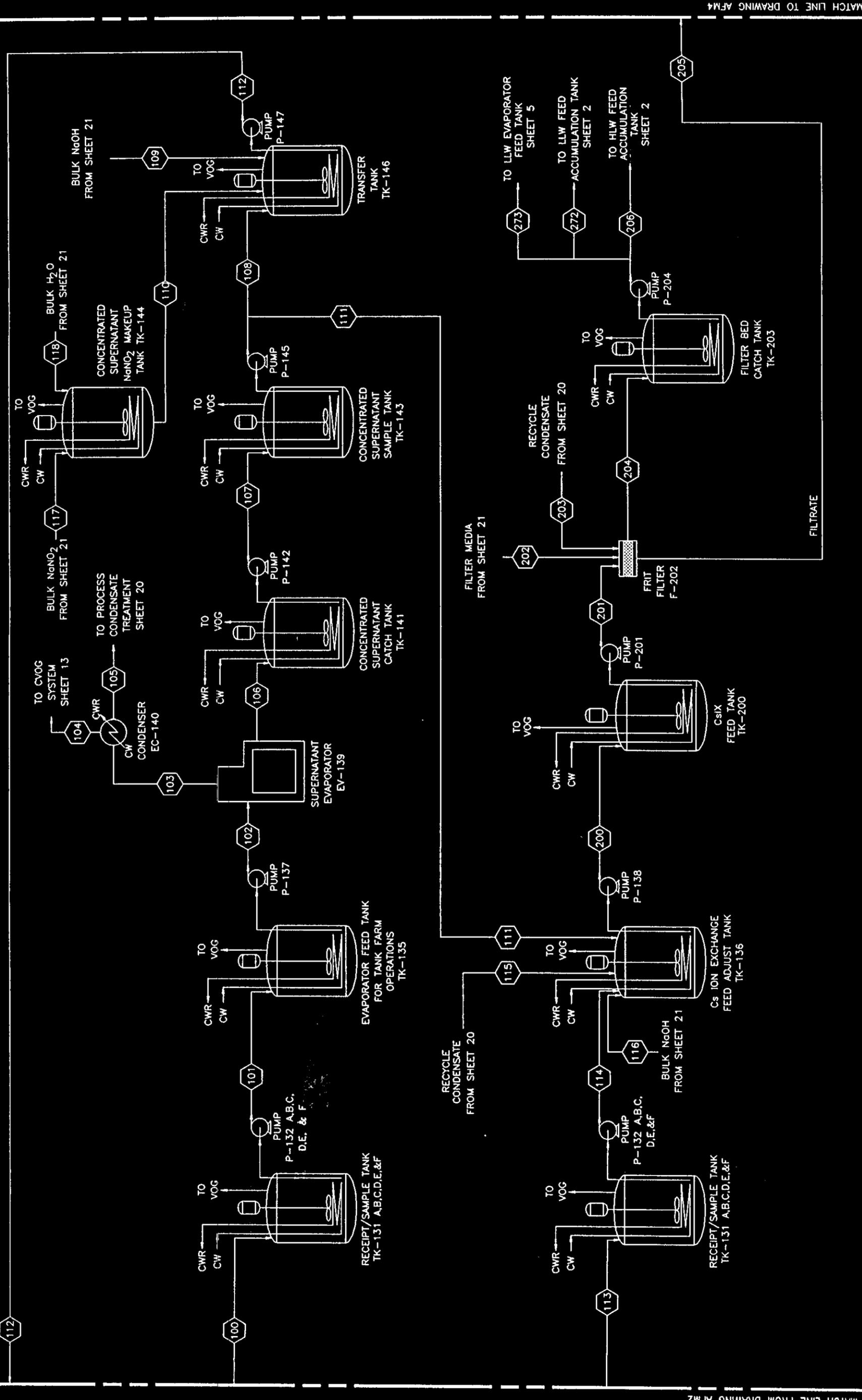
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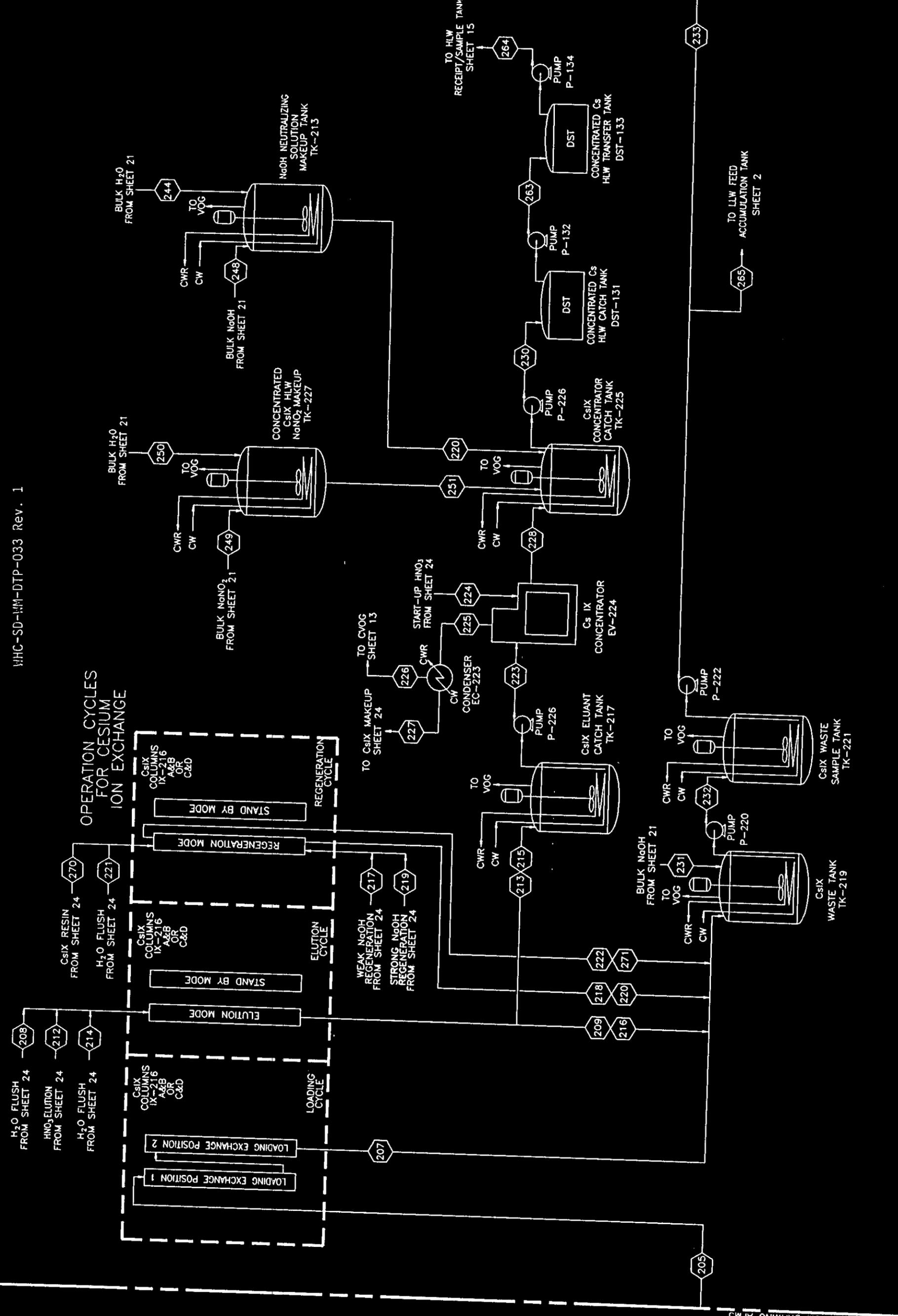


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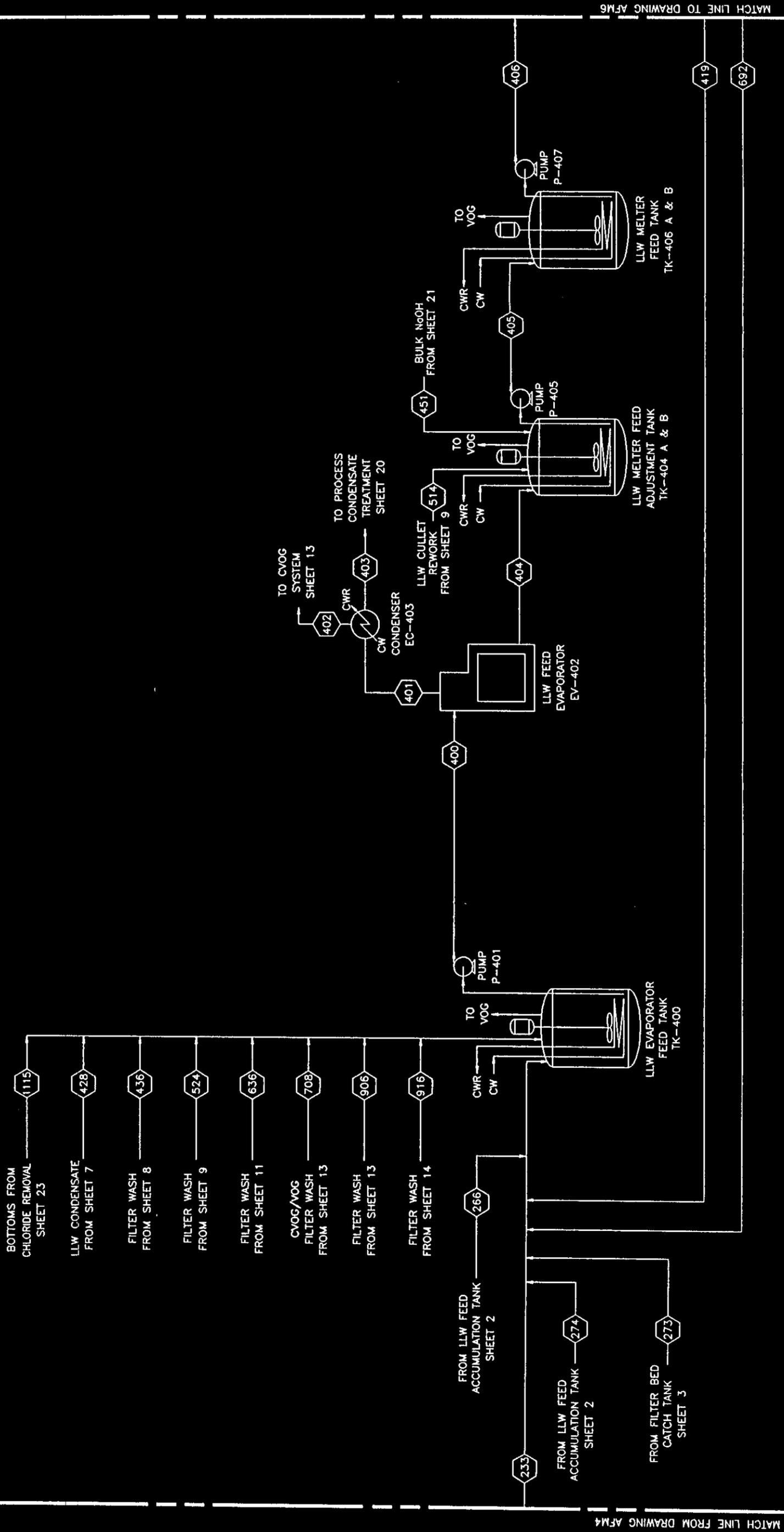
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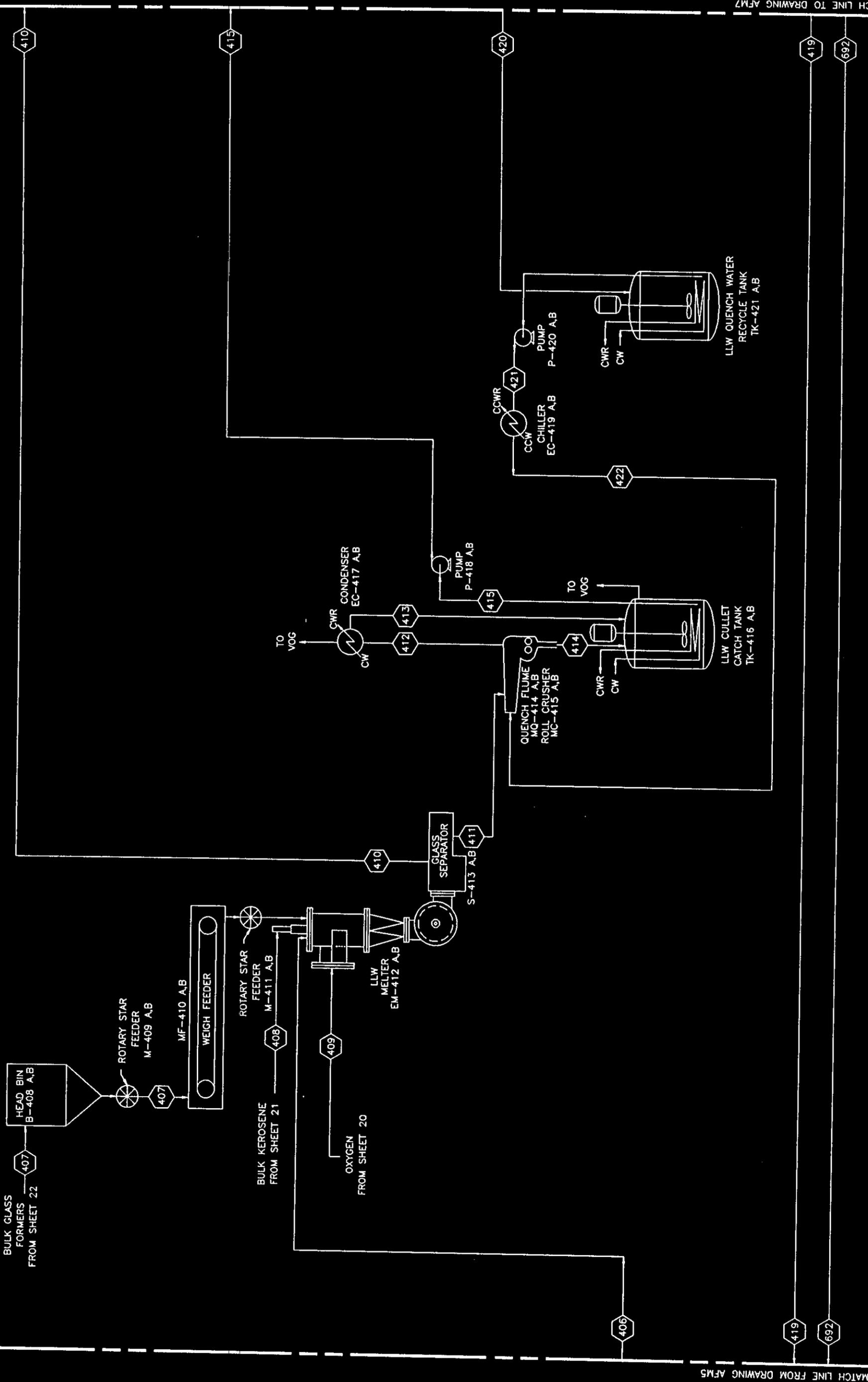
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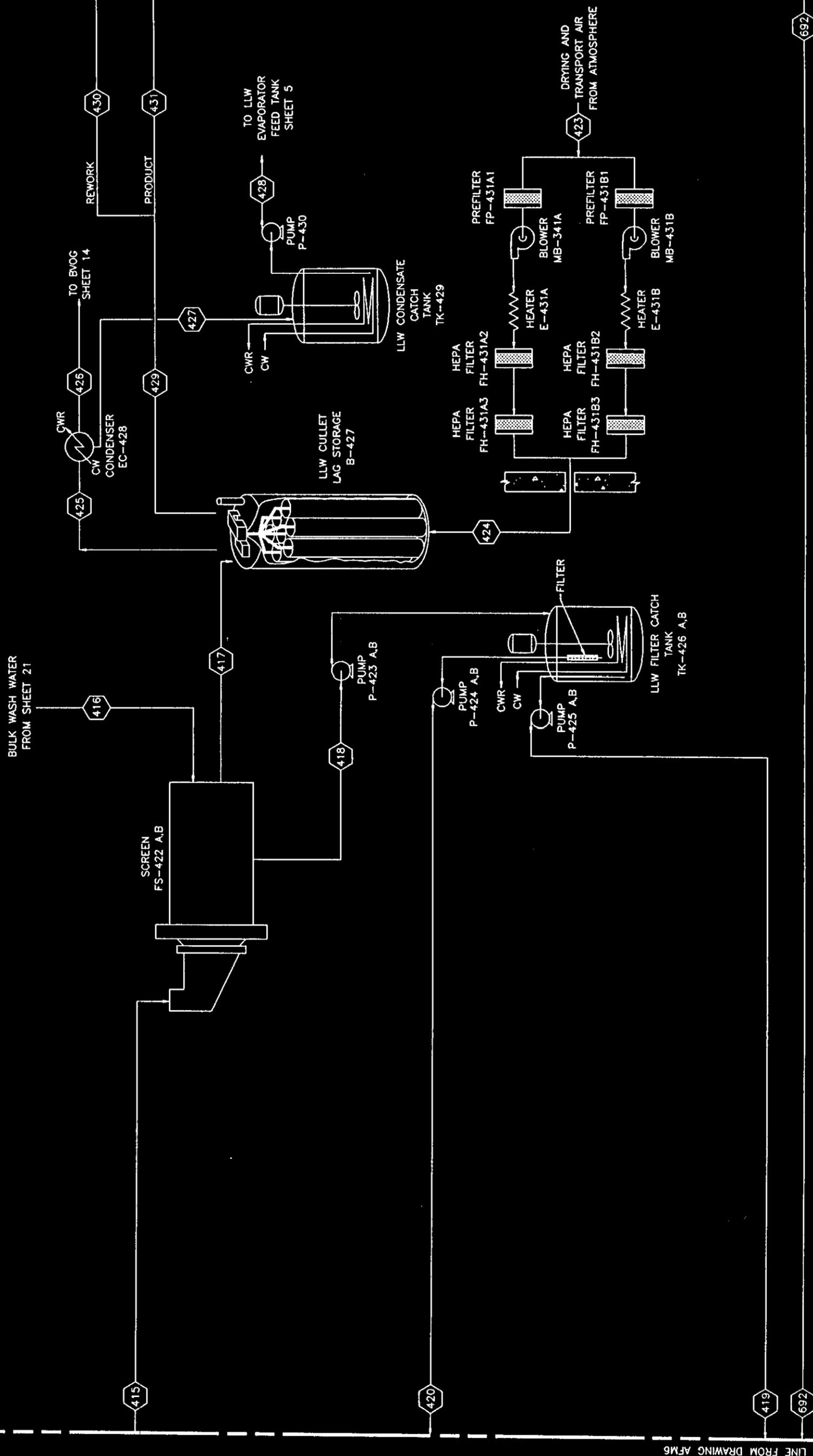
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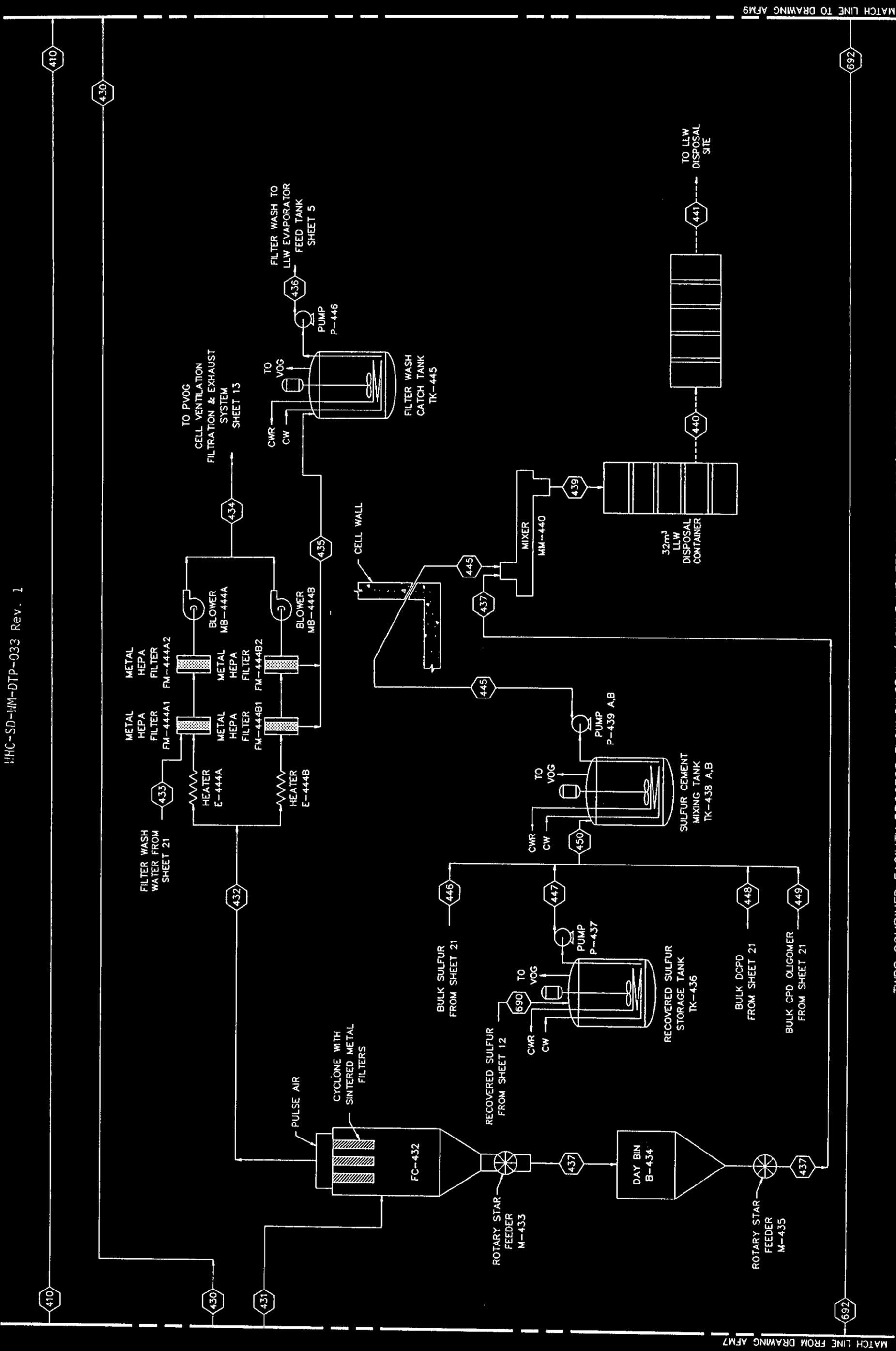
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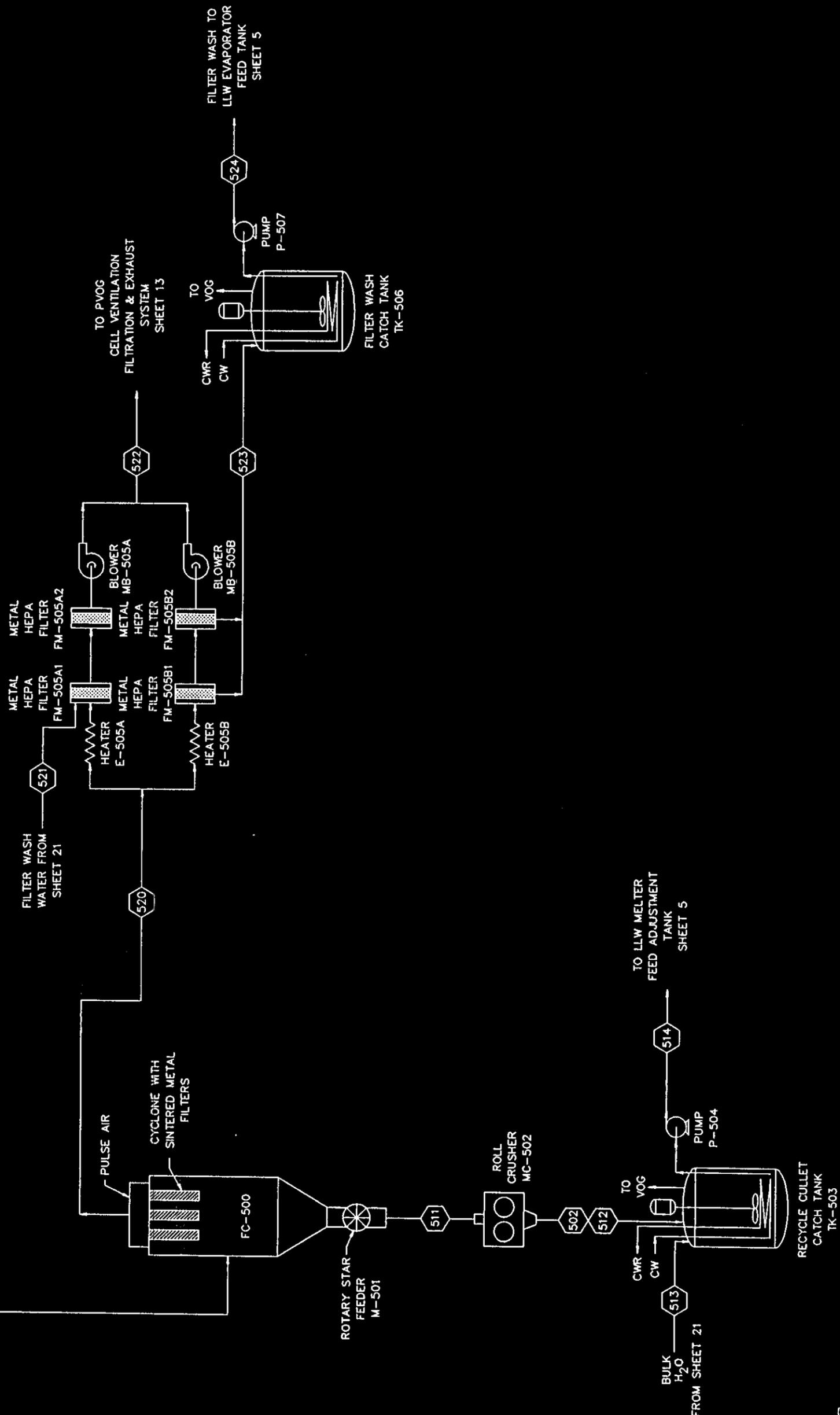
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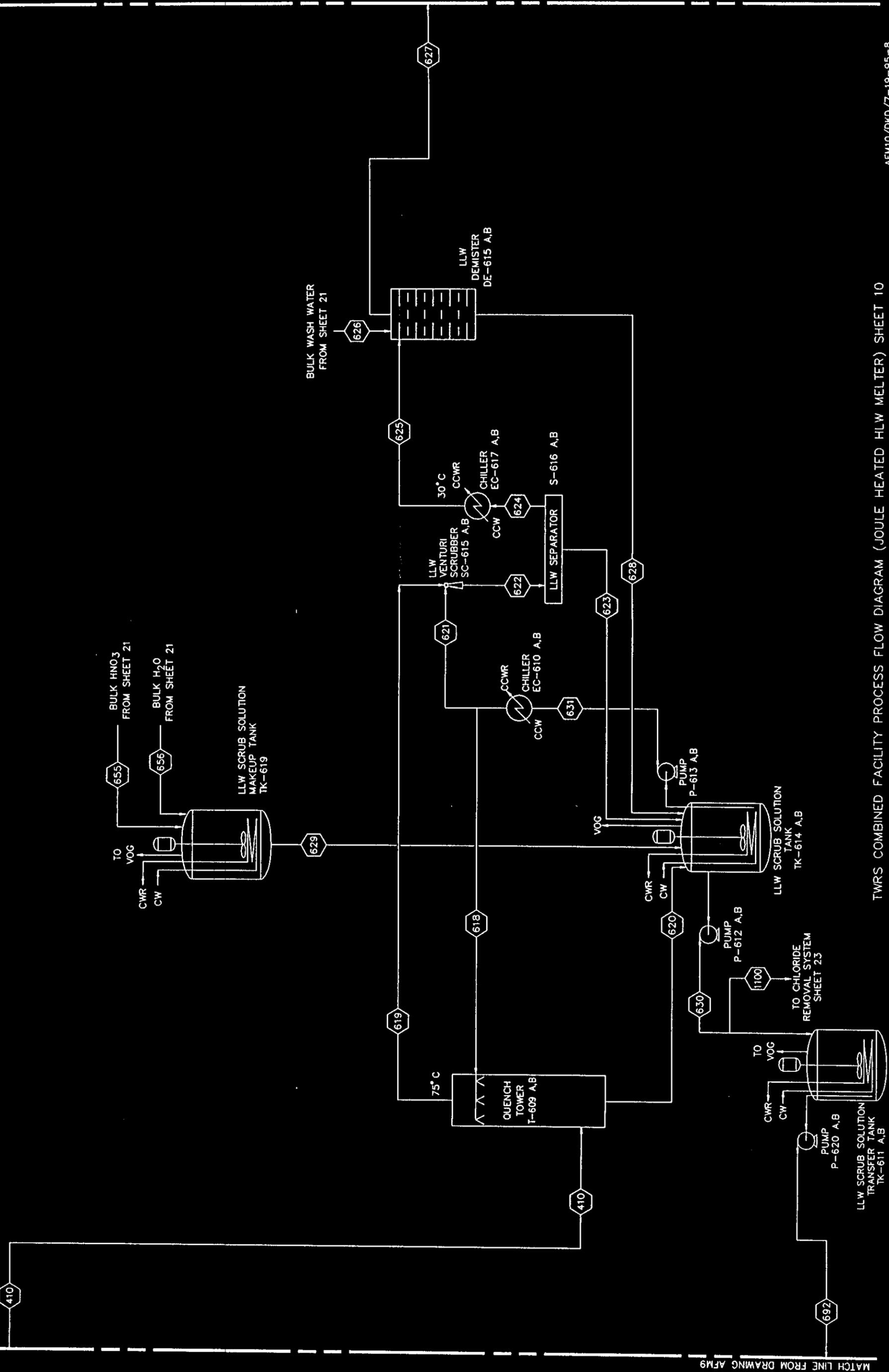
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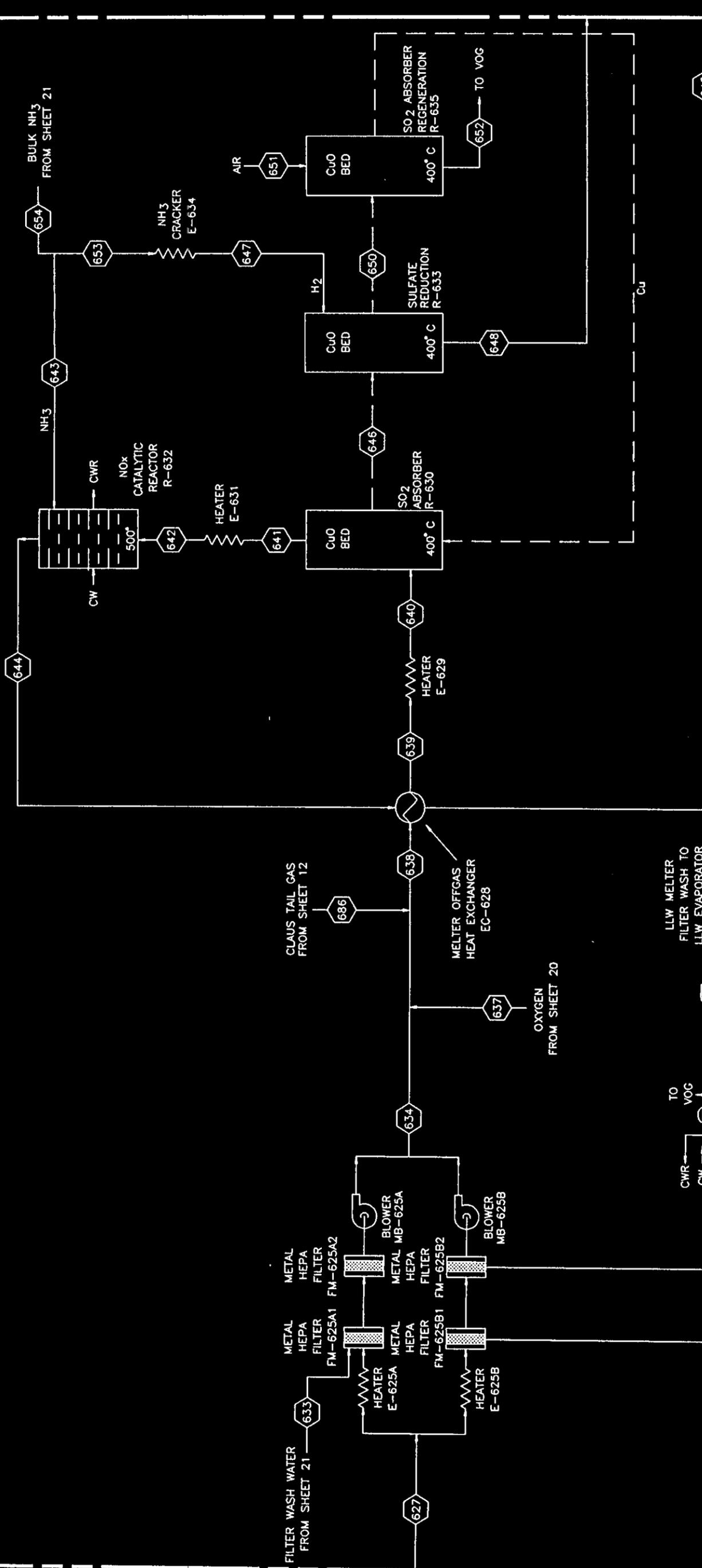
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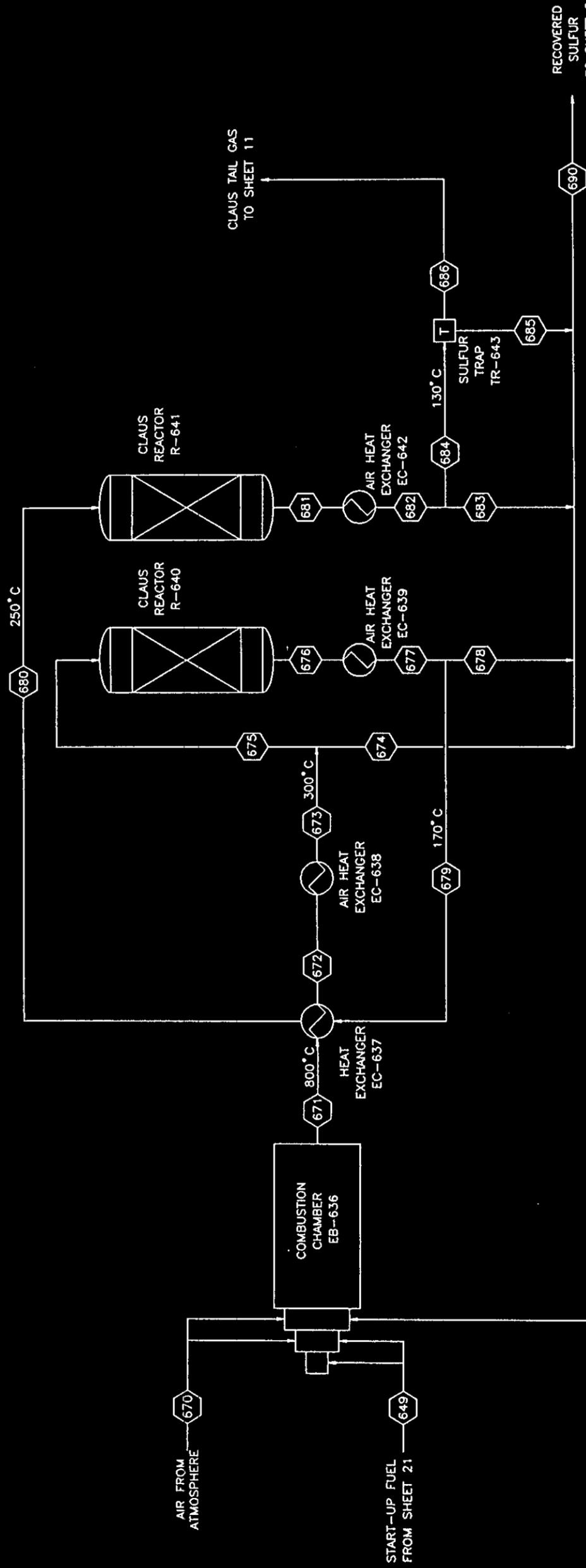
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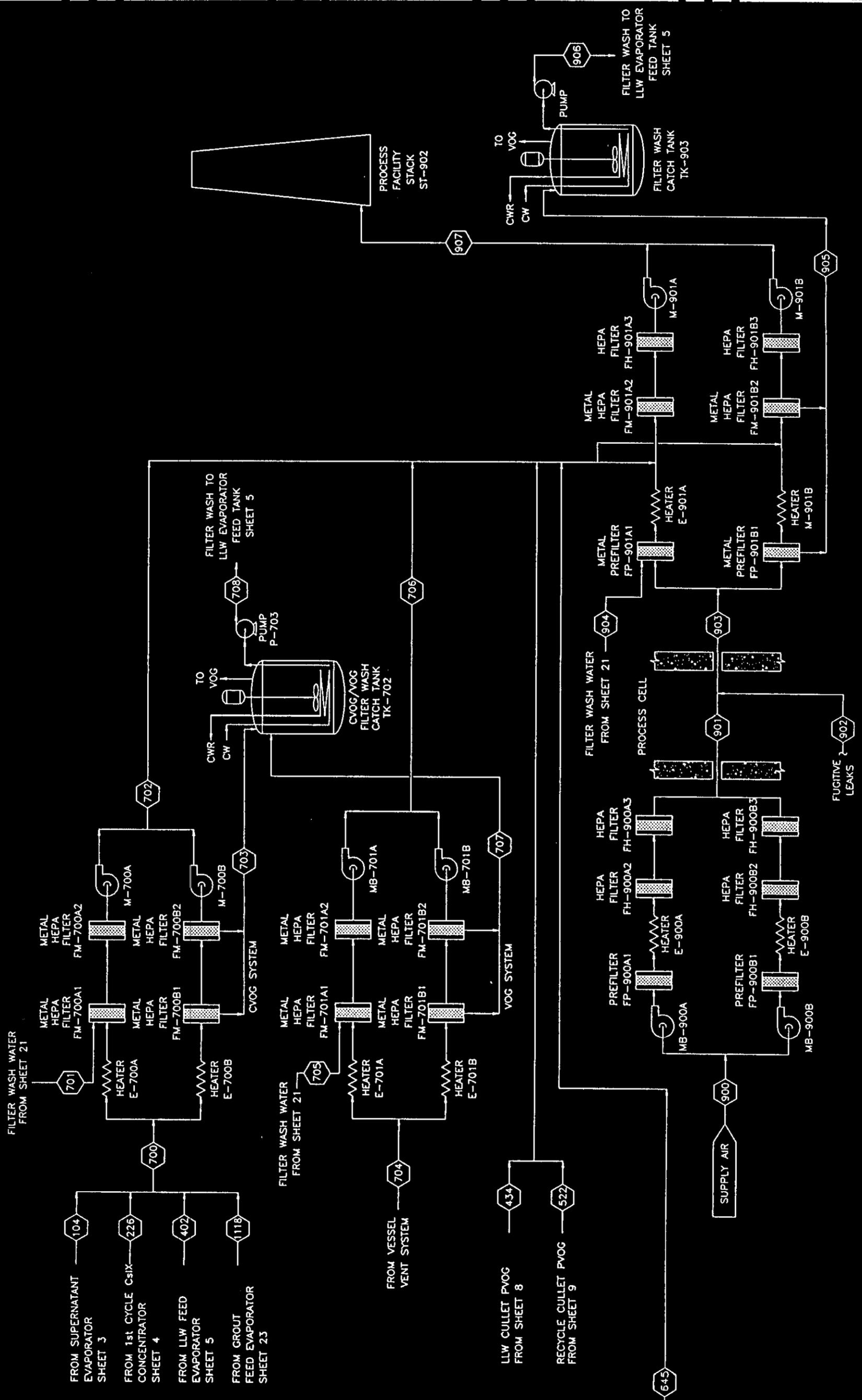
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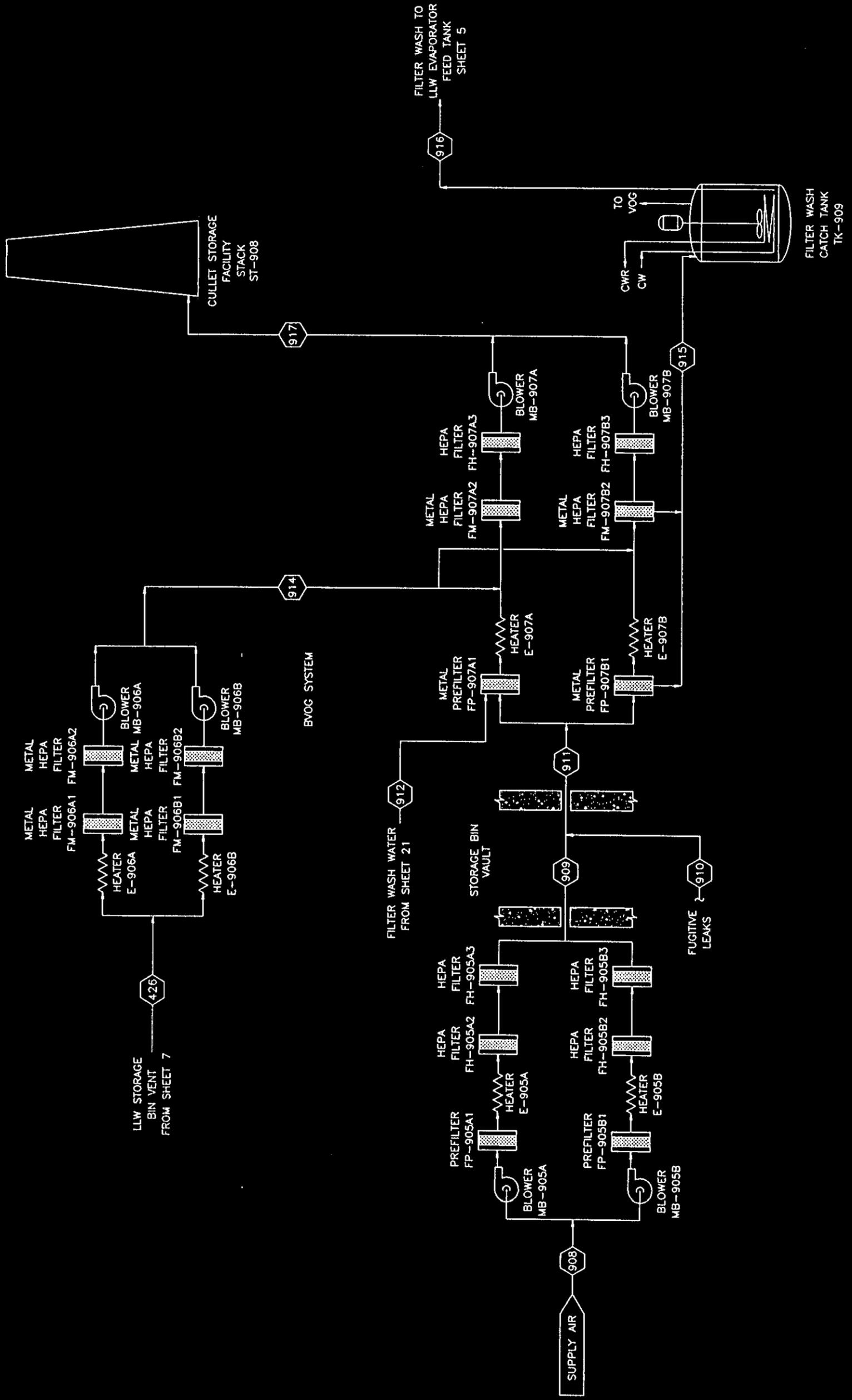
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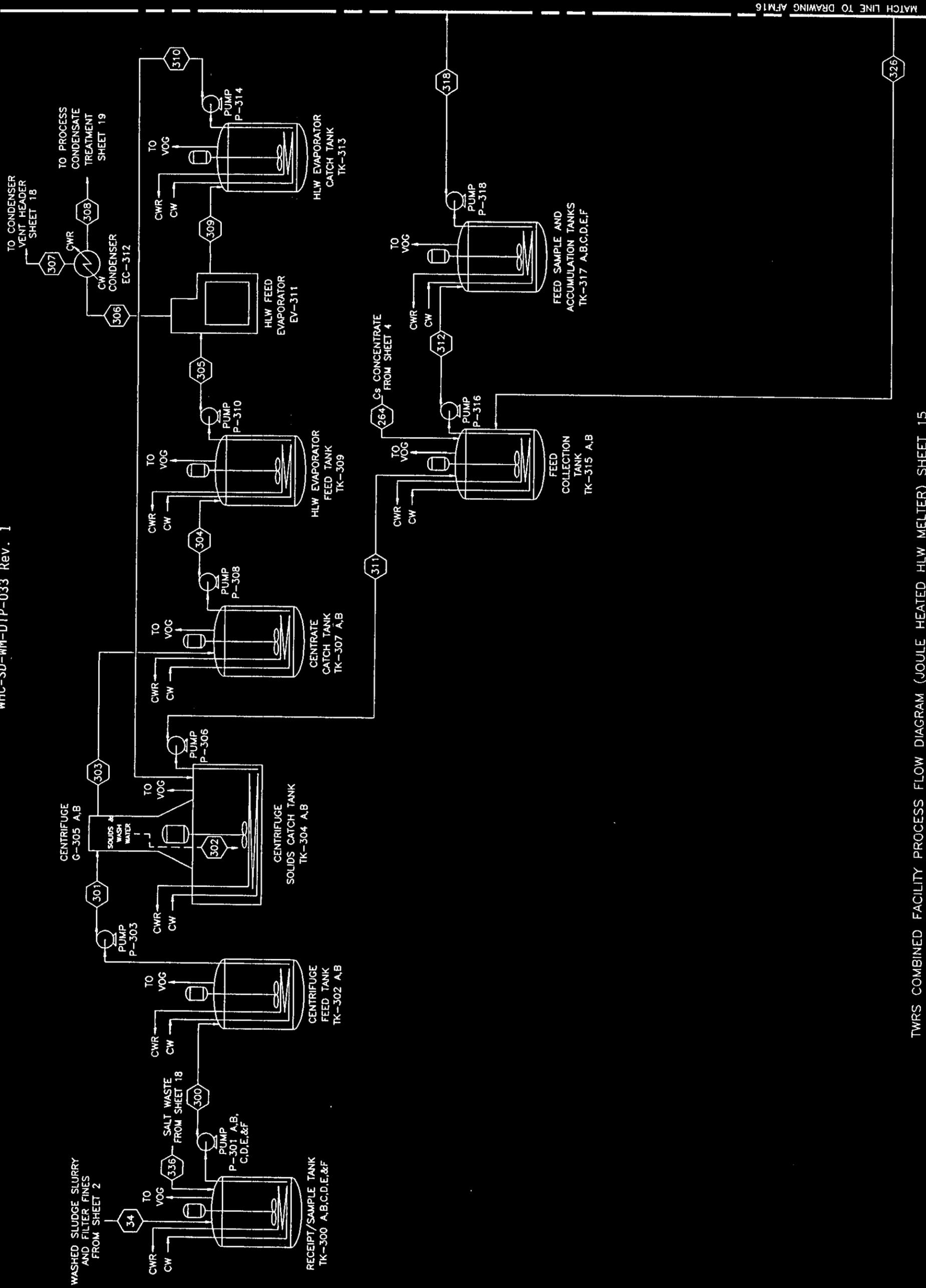
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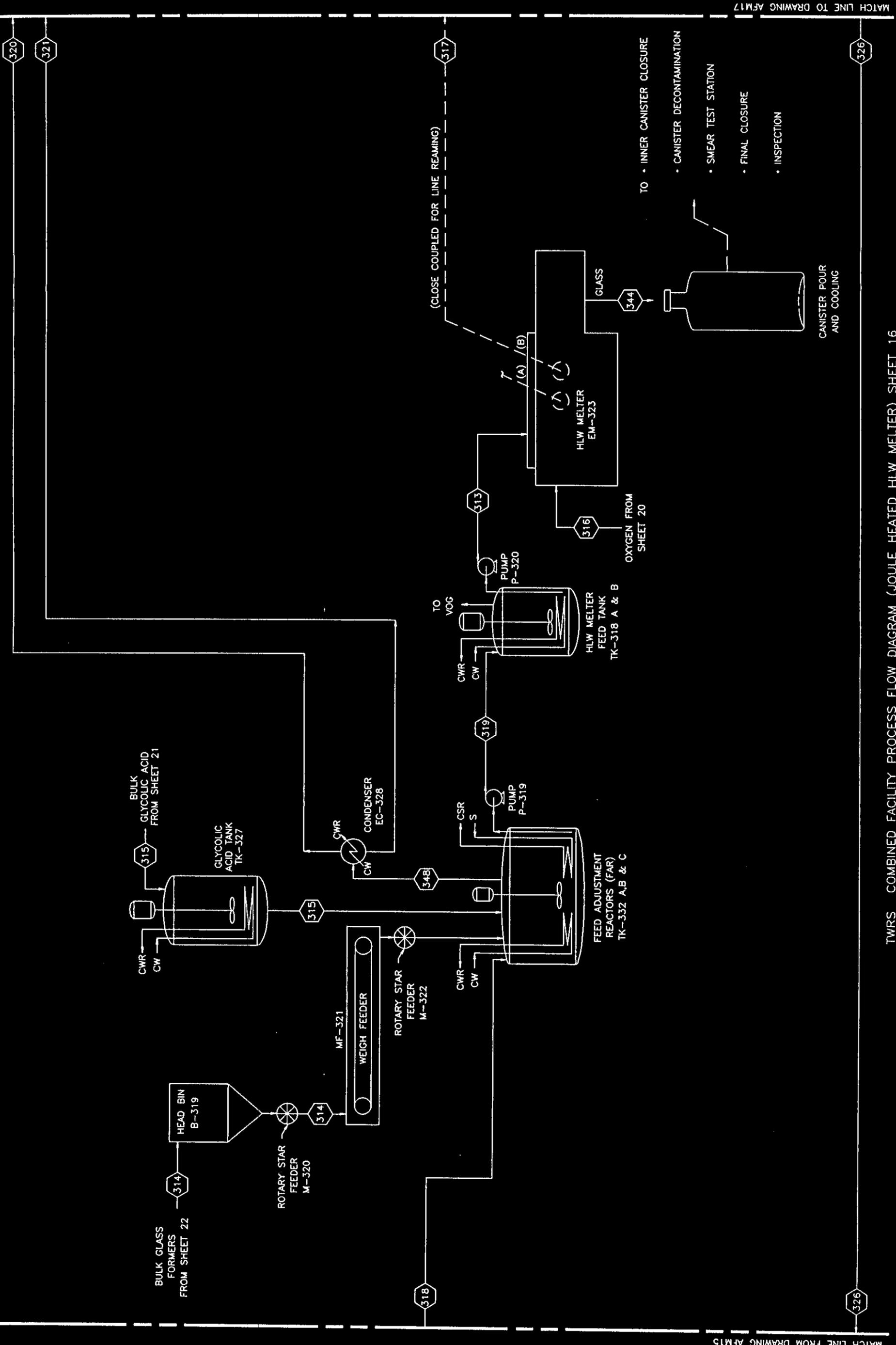
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MATCH LINE TO DRAWING AFM16

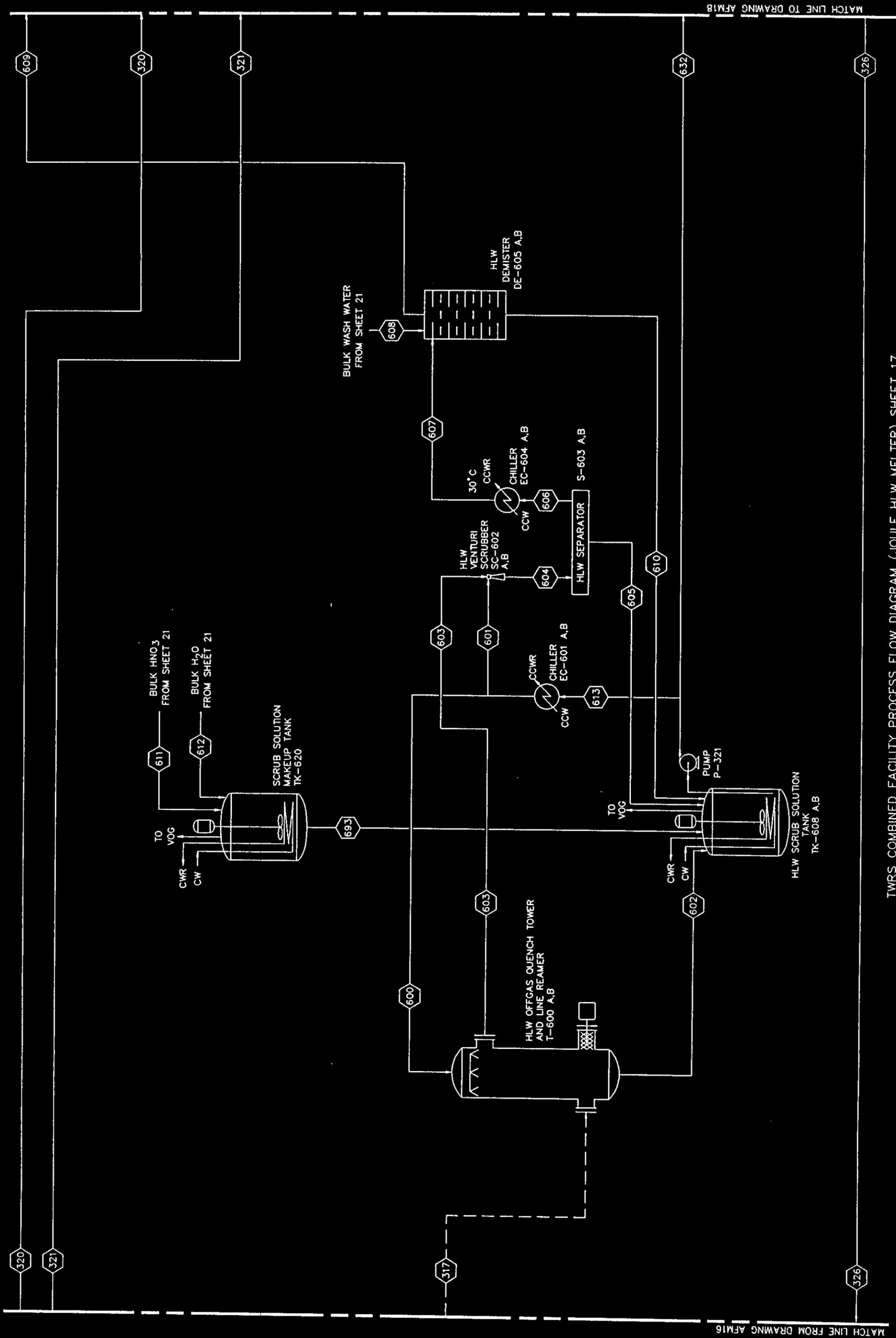
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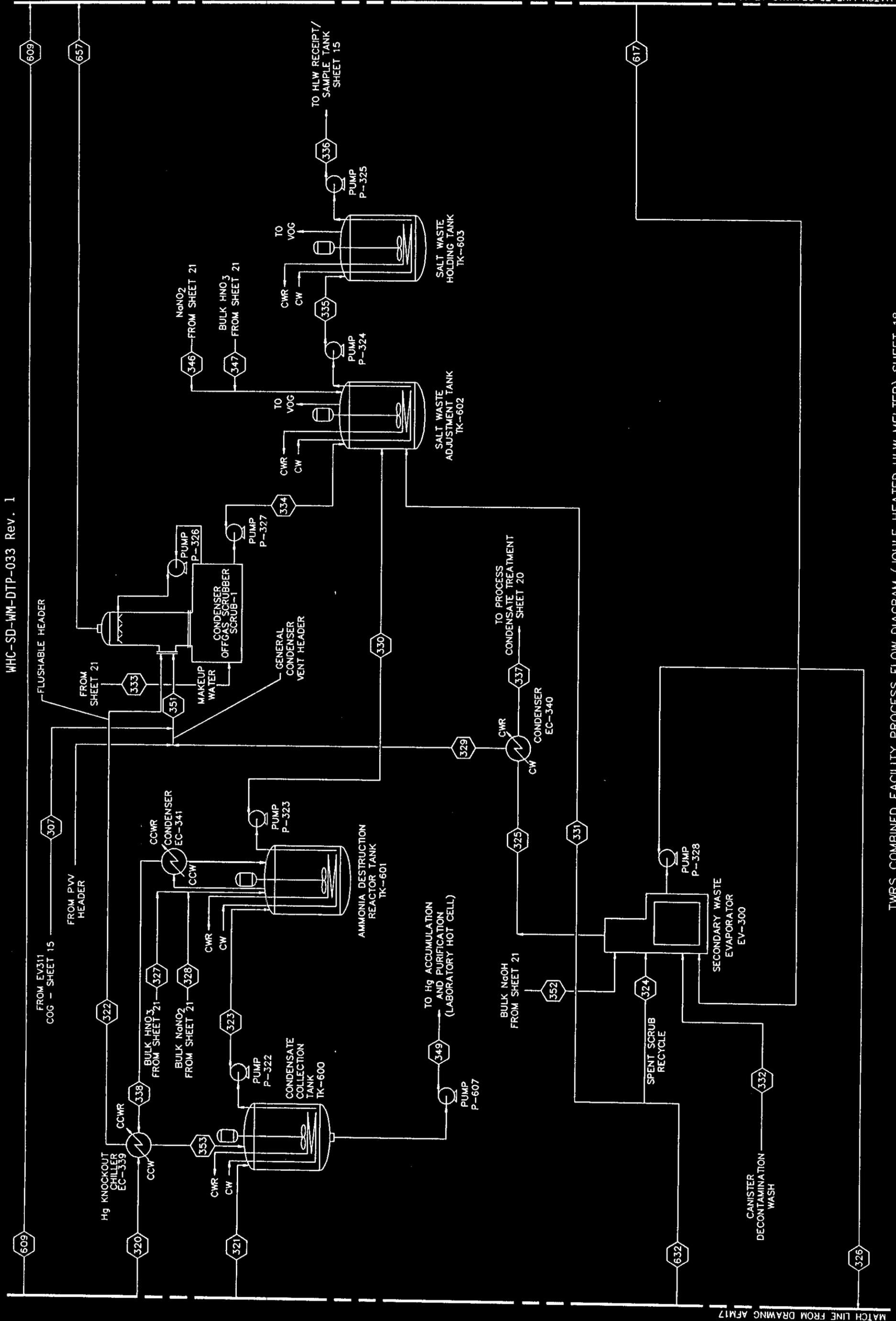
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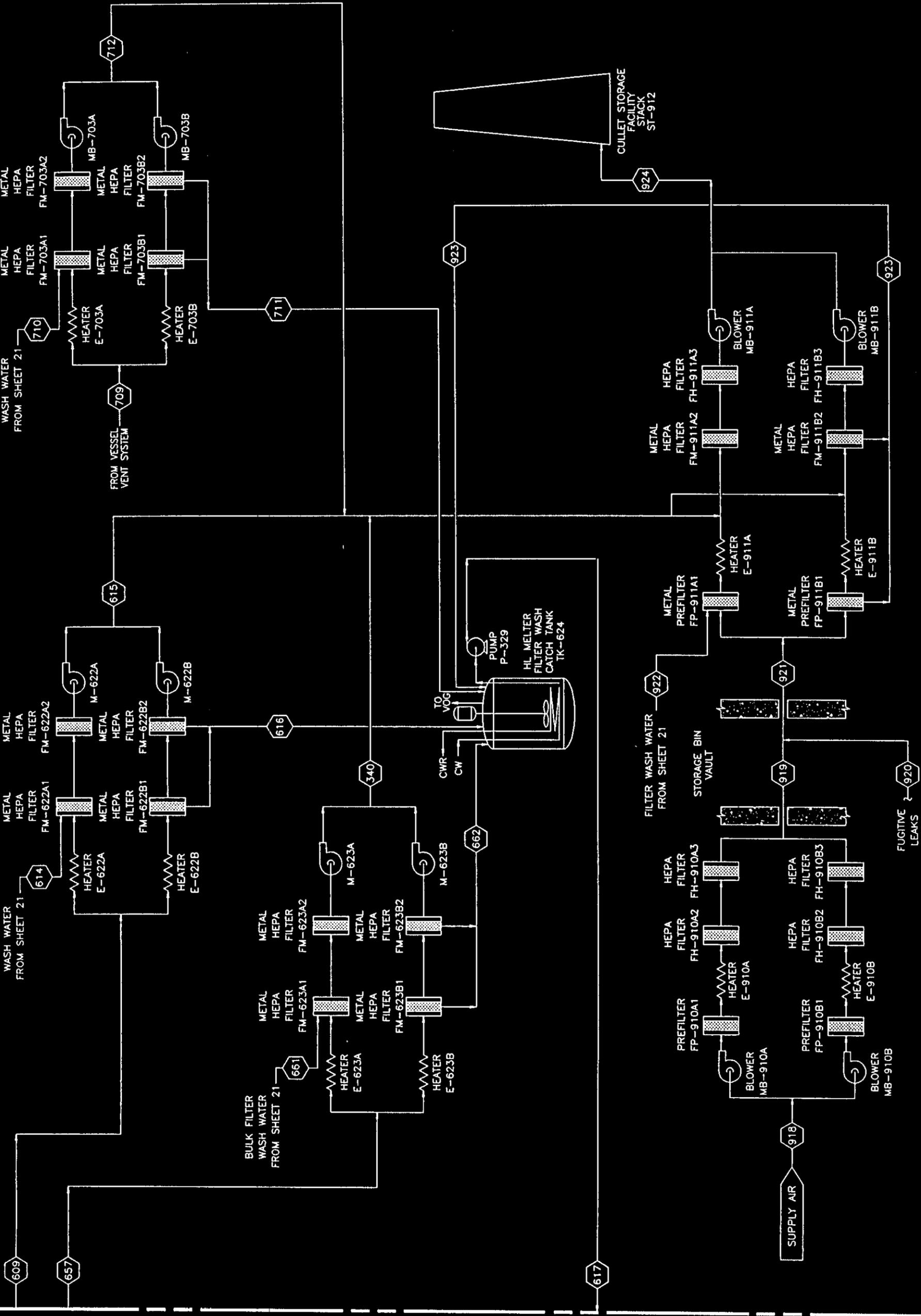
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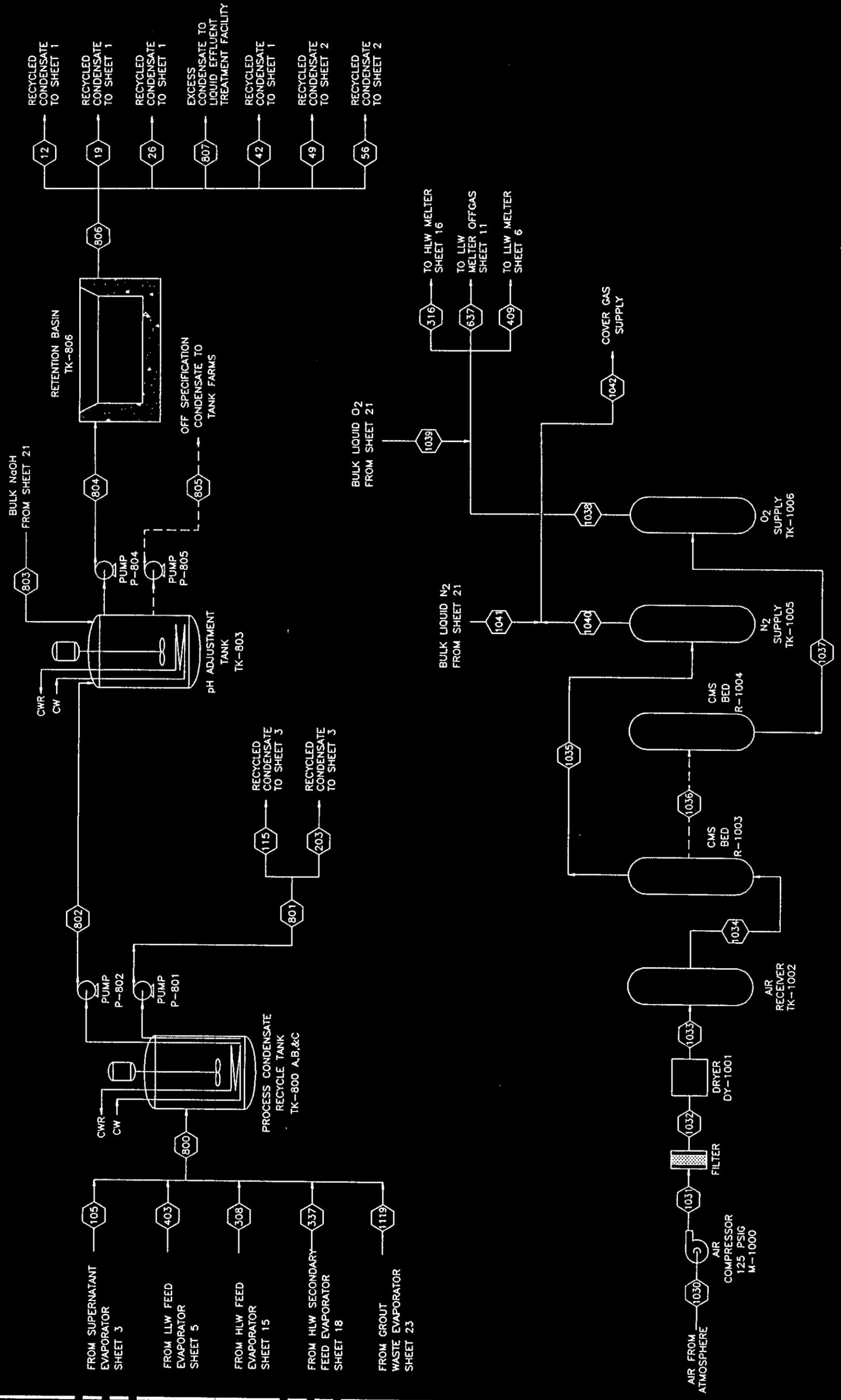
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MATCH LINE TO DRAWING AFM19

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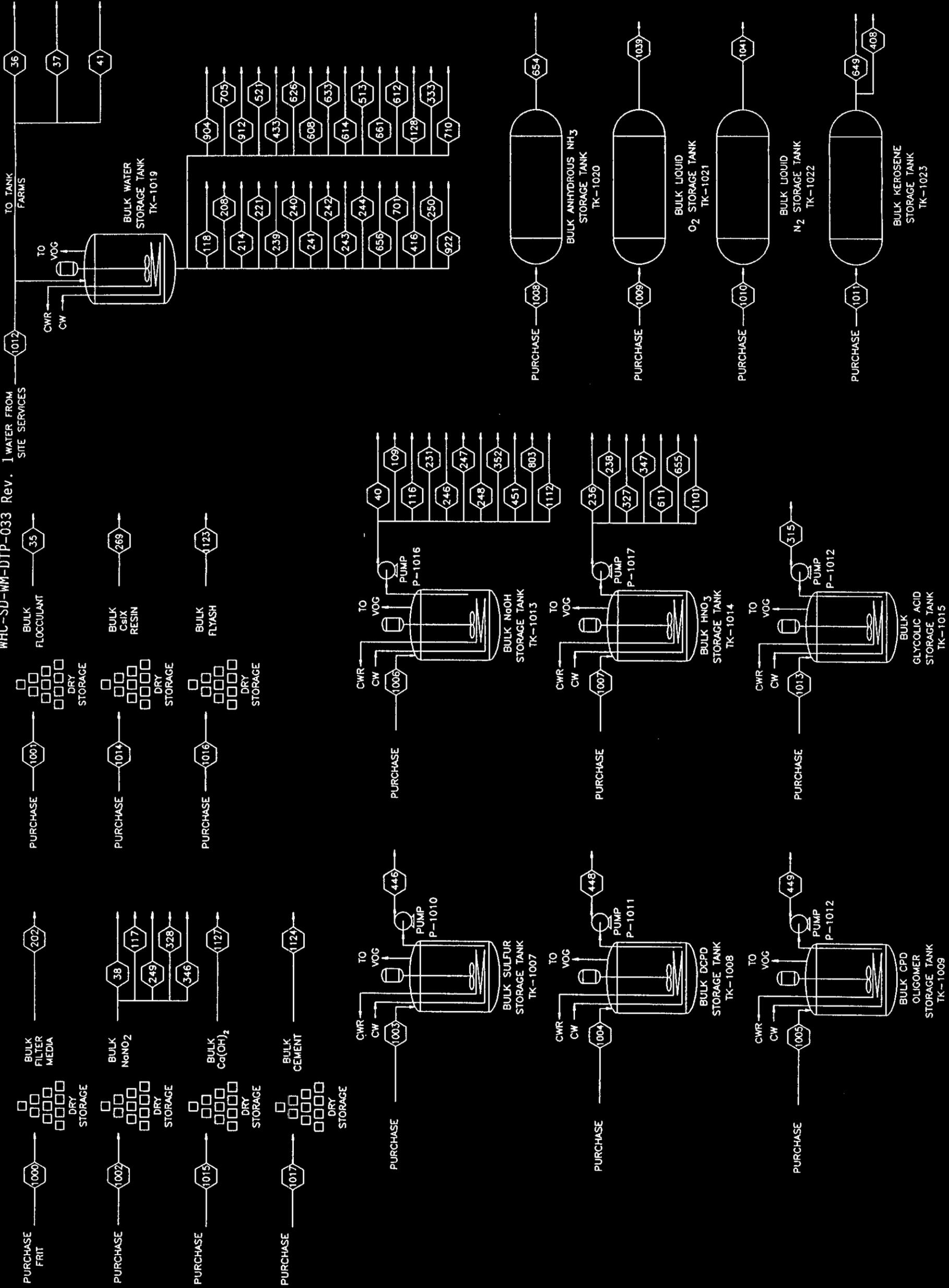


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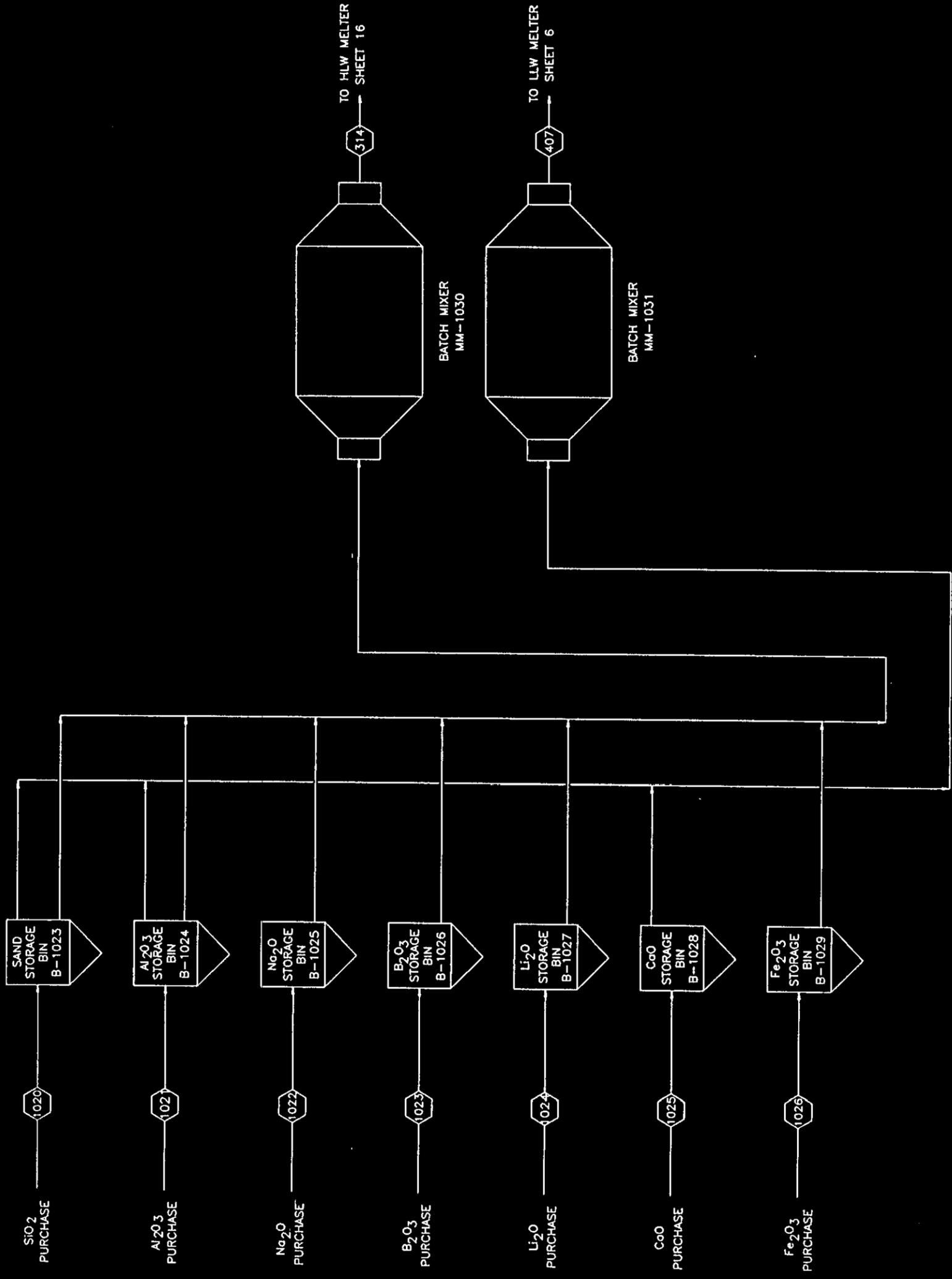


TWRS COMBINED FACILITY PROCESS FLOW DIAGRAM (Joule Heated HLW Melter) SHEET 20

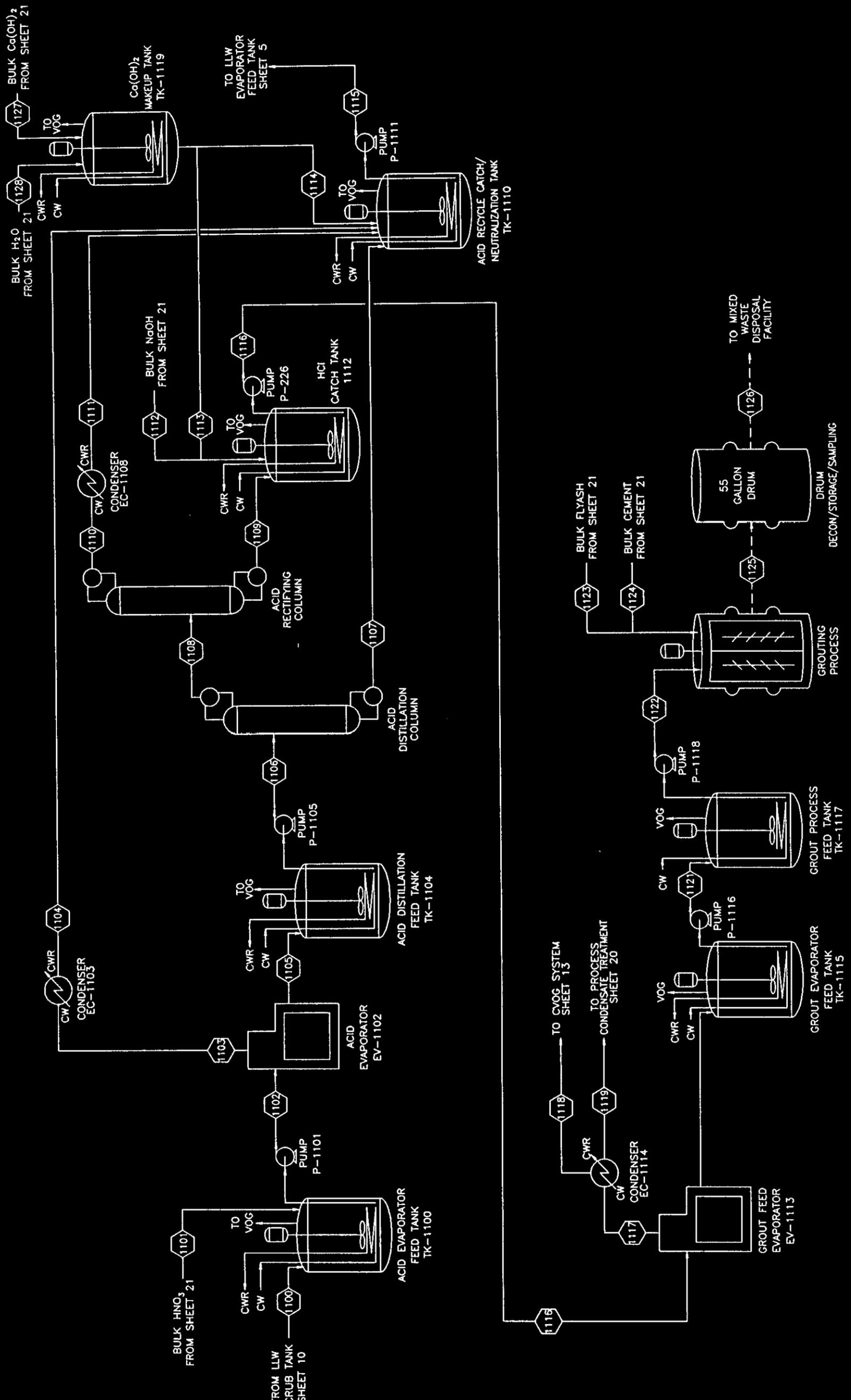
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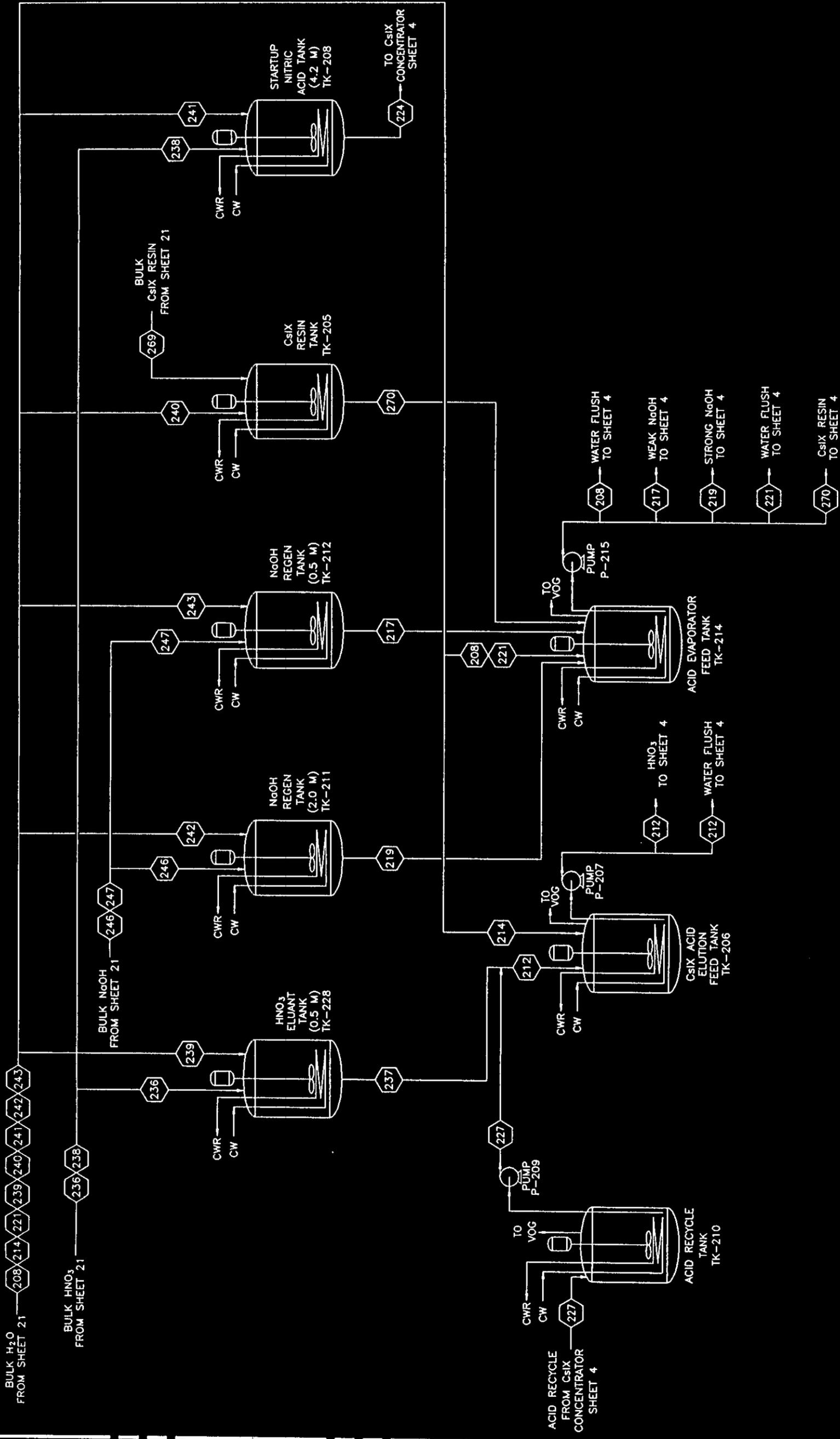
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MATCH LINE FROM DRAWING AFM22

MATCH LINE TO DRAWING AFM73

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MATCH LINE FROM DRAWING AFM72

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