

AVANTech's Innovative LLW Concentrate Treatment System Reducing Environmental Releases - 16416

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ABSTRACT

Russian Water-Water Energetic Reactors (VVER) and some Pressurized Water Reactors (PWR) utilize evaporator or reverse osmosis units to generate concentrate that must be disposed as LLRW. The new AVANTech Concentrate Treatment System (CTS™)^a was developed to decontaminate the concentrate to the point where the dry solids after evaporation are free releasable to the environment and the radioactive waste generated represents less than 3% of the original concentrate volume, thus decreasing disposal costs substantially. These concentrate solids can be recycled to non-nuclear applications or disposed as industrial waste.

Bench-scale testing has been completed with actual concentrate waste from two VVER plants with final results less than the IAEA General Safety Requirements (GSR) Part 3 discharge requirements. The VVER plants utilize chelants to conduct periodic decontamination of the piping systems that must be destroyed before utilizing precipitants and ion exchange to remove most of the isotopes.

INTRODUCTION

The objective of AVANTech's CTS™ is to treat either evaporator or reverse osmosis concentrates to minimize radioactive volume while producing a maximum quantity of non-radioactive disposable waste or recyclable material.

There are many variations of this system depending on influent and location constraints on the disposal stream. Discussed herein are the most extreme conditions which may not apply to every installation. The VVER plants evaporate concentrates are highly alkaline, high salt, and have high boron concentration containing chelates.

Also discussed are the major sub-systems of the CTS™ that could consist of the following:

- Oxidation System
- Sorbent and Filtration System
- Ion Exchange System
- Evaporation System

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The CTS™ process is based on meeting the IAEA Safety Standards, GSR Part 3, to which most European countries comply. AVANTech's CTS™ is flexible for a number of different plants that may have different environmental conditions and constraints. That means not every aspect of the process needs to be utilized in all applications. The final pathway can be either discharge of a liquid or a solid stream depending upon both isotopic and salt discharge constraints.

Depending upon whether final disposal may be discharge to the ocean, discharge to an inland body of water, or recycle back to the plant, variations in the required portions of the system may apply to a given location. For example, an ocean discharge may not require the removal of alpha isotopes and may allow the direct discharge of boron and other nonradioactive salts.

DESCRIPTION

Figure 1 (next page) depicts a block process flow diagram of the CTS™. The block diagram shows the flow paths, and the process loops related to the major components or process steps are displayed with the discussion for easy reference.

The Oxidation System addresses destruction of organics, such as chelants that may hold the isotopes strongly, and oils or other organics that may interfere in downstream processes. Ozone is the desired oxidant due to its very high oxidation potential and requires no handling of other chemicals. The temperature and pH adjustment are used to enhance this process.

The next step is the use of powdered sorbents to make many orders of magnitude reduction in the high activity isotopes, usually cesium (Cs) and antimony (Sb). Powdered sorbent reduce the waste volume by about an order of magnitude from the use of ion selective media while maintaining a cost and volume effective alternative. Usually either two or three treatments are required to obtain the optimum results. The sorbents are maintained in a suspended state through mixing. The small volumes of sorbents representing 0.1-0.3% by weight of the feed stream are sufficient to reach these results. The solids are then removed by a hydrocyclone, and any residual solids are removed using ultrafiltration.

The final step in removing the remaining dissolved isotopes is the use of ion selective media for several of the isotopes. The effluent goal is to reach 1-2 Bq/L of the major gamma isotopes. The concentrate is then collected in a monitor tank for analysis prior to either discharge or evaporation.

Finally, if evaporation to dry solids is the desired final product, a combination of thin film evaporator and continuous mixer drying is employed to assure complete removal of tritium (H-3) and carbon-14 (C-14), if present. This also means adjusting down the pH in some applications.

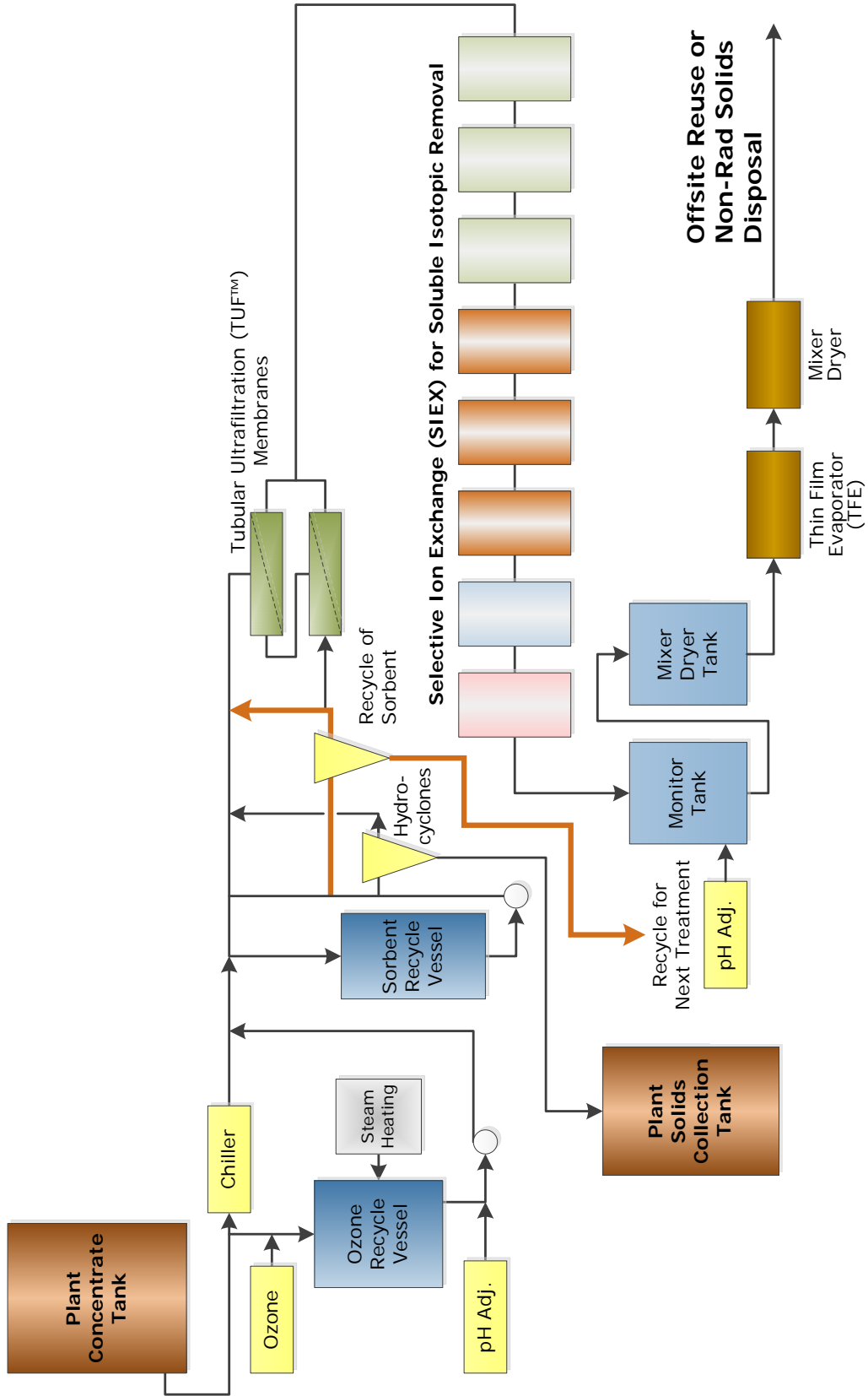


Fig. 1. Concentrate Treatment System (CTS™)

DISCUSSION

Feed Stream with Chelants or High Organic Content

If organics are not an issue, then one may proceed to Sorbent Treatment.

a. Cooling and pH Adjustment

Chilling to $<25^{\circ}\text{C}$ and pH adjustment to ≤ 11 is required to speed the oxidation process. The cooling permits higher solubility of ozone in the concentrate, and lower pH aids in the reaction rate of the ozone in attacking the chelants in later steps.

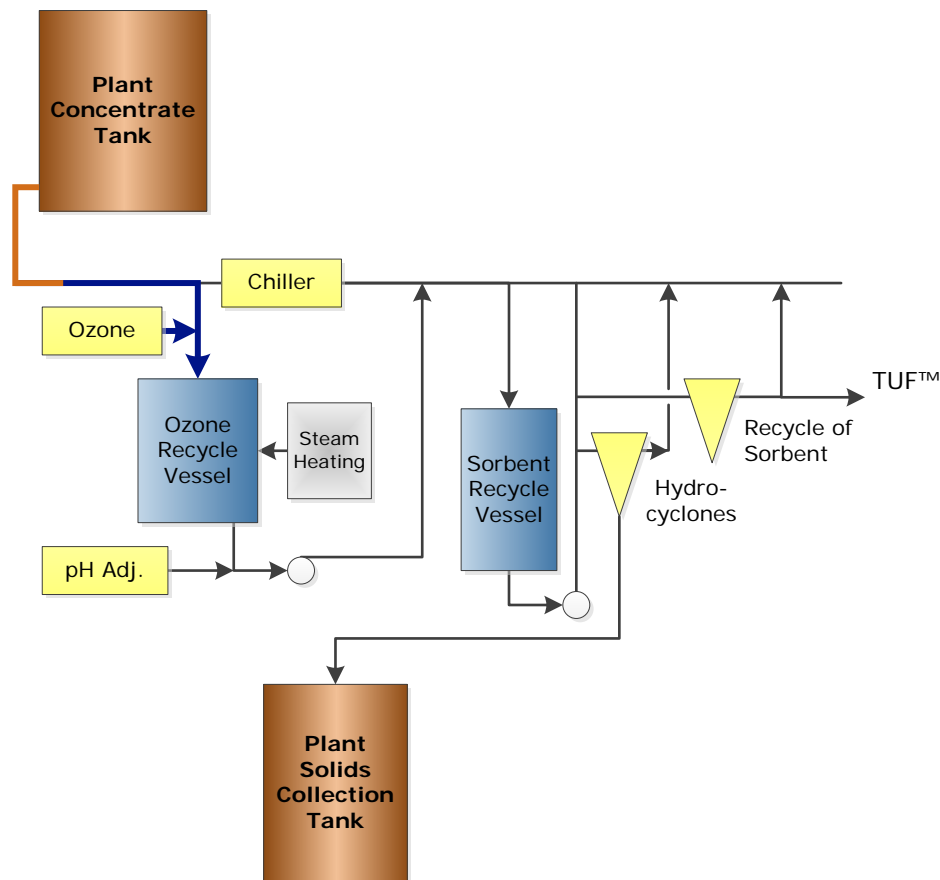


Fig. 2. Concentrate Cooling and pH Adjustment

b. Ozone – Oxidation Pretreatment System

Ozone pretreatment, crucial to processing success, destroys the chelants and other organics present in the feed stream, which releases chemically bound radioisotopes and protects the downstream membrane system from fouling. Ozone is a powerful oxidant that can attack and destroy the chelants and other organic fouling agents. The oxidation products are principally carbon dioxide (CO_2) and water, leaving no

residual secondary chemicals in the waste stream. Complete destruction of all organics containing C-14 may be required to meet effluent requirements.

Destruction of organics and oxidation of any of the isotopic corrosion products causes some isotopes, such as cobalt (Co), to precipitate. The organics of most concern are the chelants present from decontamination operations. Ozone's very high oxidation potential is able to attack and destroy these chelants during pretreatment. The destruction of the chelants releases the bound radioisotopes, facilitating their eventual precipitation and filtration, or ion exchange.

Figure 3 shows the Oxidation Loop that operates until the organic inventory has been destroyed. To facilitate maintenance of the recirculating process fluid in the optimum temperature and pH range based on testing, the recirculation loop is equipped with a chiller system and an in-line pH adjustment system to maintain the process fluid in the optimum range to enhance oxidation.

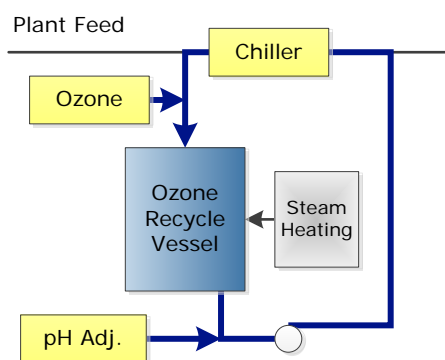


Fig. 3. Oxidation Loop

The initial pH of the feed concentrate is reduced to a pH of <11, thus increasing both the rate of oxidation and the ability to oxidize the most difficult organics. Nitric acid is used to lower the pH, which is measured by the in-line pH probe.

The ozone is produced from dry compressed air that is separated by pressure swing absorption (PSA) into about 93% pure oxygen. The produced ozone is introduced to the Ozone Recycle Vessel through the recirculation system by an eductor and further mixed by a high intensity mixing process to maximize contact opportunity between the ozone and targeted organic material, maximizing oxidation. The oxidation process continues until all chelants are destroyed, as indicated by an elevated Oxidation-Reduction Potential (ORP) reading, usually in the range of +500 to +1000 mV.

In this ORP range, the final completion of destruction of the chelants is signaled by a further decrease in the pH caused by resumed generation of excess CO₂ from the broken carbon chains of the oxalic, citric, and ethylenediaminetetraacetate (EDTA) chelants. Although complete destruction of these organics is not required, the ability to assure removal of essentially all C-14 requires that 100% of the organics be destroyed, converting them to CO₂.

The temperature is also taken to as high as 50°C (120°F) to increase the rate of re-dissolution of any precipitated boron, if present. Depending upon the expected final concentration of boron in the waste, some additional dilution may be required to assure that no precipitation occurs during the remaining processing steps. Any precipitation would not be ideal as the water must later be removed through evaporation, so an increase in temperature is preferred.

Sorbent Application and Ultrafiltration

Sorbents are used to target two primary isotopes: Cs and Sb. The Sorbent Recycle Vessel has several recirculation paths depending on the particular operating stage and the desired process outcome. A simple recirculation loop that bypasses both the Hydrocyclone and the Tubular Ultrafilter (TUF™)^b (shown in Figure 4) was incorporated into the system.

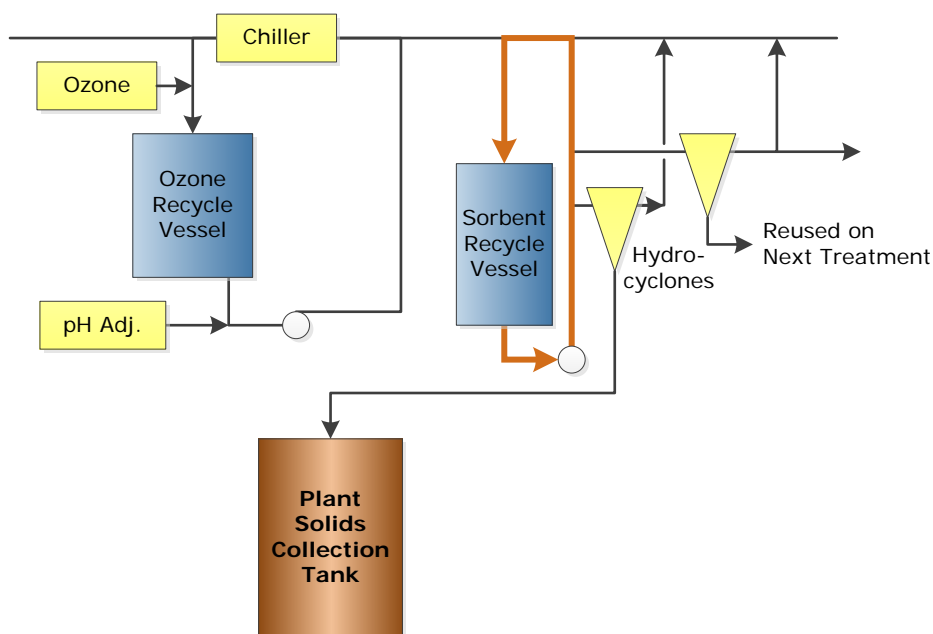


Fig. 4. Sorbent Treatment and Removal Loop #1

This provides for complete utilization of the sorbent media that fall into the outlet at the bottom of the conical tank. A combination of the mixer in the tank and periodic recirculation may be required to fully utilize the sorbent capacity. The mixer is engaged and the recirculation pump cycled on periodically to keep the sorbent in suspension for maximum sorbent-waste contact.

Testing showed that the optimum sorbent application was to apply the Cs and then the Sb sorbents sequentially. This also assists analysis as Sb is often hidden by the Cs peak.

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Testing has shown that the addition of a second dose of Cs-specific sorbent is effective at reducing activities by another 1-2 orders of magnitude without using much of the potential capacity. This means the sorbent can be used a second time without any apparent effect on capacities or decontamination factor, thus reducing the amount of sorbent used by half. For this reason, a second Hydrocyclone and interim storage tank were added to permit storage of the Cs sorbent for use on the next batch.

The Hydrocyclone (shown in Figures 1, 2, 4, and 5) was incorporated into the system design to facilitate removal of solids from both the initial concentrate feed and added residual sorbents after sorbent treatment. The initial Hydrocyclone was removed from the Ozone System when it was discovered that the concentrate contains several percent of solid sodium borate. If this sodium borate is removed with corrosion products, the volume of solid waste that normally is <2% for sorbents might increase to >5% because of these solids. By removing the Hydrocyclone at the front of the system, these sodium borate solids are then re-dissolved as one of the steps in the Ozone System process, so they are eventually sent to the Mixer Dryer for final disposal as clean industrial waste.

A second Hydrocyclone was added to the TUF™ System to enable removal and recycle of sorbent solids that are used in a second sorbent treatment using the same sorbent material. Since such a small portion of the sorbent is utilized, the reuse on the next batch of concentrate produces essentially the same result as treatment with fresh sorbent. This decreases the usage of sorbent by 50%.

The Hydrocyclone removes and concentrates the solids to a form that can easily be transferred to the Plant Solids Collection Tank on a batch basis. The Hydrocyclone uses the centrifugal force of the liquid spinning at a high rate of speed to throw the heavier particles to the outside where they fall to the bottom of the cone and into a quiet zone. This minimizes the amount of liquid that is required to do the transfer.

When the bulk of the sorbent has been removed by circulating through the Hydrocyclone, the process fluid is routed through the TUF™ System. The TUF™ is used to remove all the remaining particulate solids, both isotopic and non-isotopic, from the process stream, as shown in Figure 5.

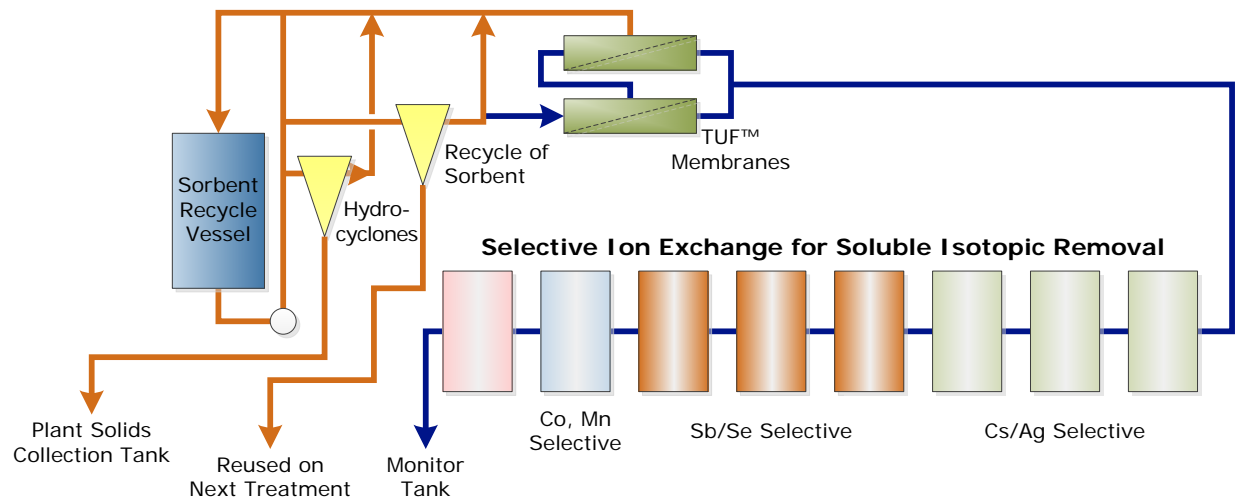


Fig. 5. Sorbent Treatment and Ultrafiltration

Many of the isotopes, such as Co, manganese (Mn), chromium (Cr), iron (Fe), silver (Ag), and others, are often found primarily as oxide and carbonate solids, making them excellent filtration targets. Though the Hydrocyclone removes up to 99.9% of the solids, to achieve the process goal of <5 Bq/L activity levels for isotopes, removal of all particulate is necessary.

The TUF™ is an effective means of filtration down to a 20,000 molecular weight (M.W.) cut-off, or approximately 0.02 μm . The TUF™ consists of a series of membrane modules in series and parallel. The wastewater is pumped through the tubes, and the filtrate is collected in the space around the tubes. Unlike typical dead-end mechanical filters, the TUF™ membranes are cross-flow by design. The high velocity of the water circulating through the membranes continually scours the face of the membranes clear, thus preventing solids from accumulating and fouling the membranes.

The M.W. cut-off was reduced from the previous 100,000 M.W. to 20,000 M.W. to assure removal of all particulate isotopes such as Co and Ag-110m.

Selective Ion Exchange System

The Selective Ion Exchange (SIEX) System, shown in Figure 5, is designed as a polishing unit using ion selective media. Selective exchange media are specially designed to target specific radioisotopes for removal while allowing the bulk of the non-radioactive species, such as sodium, chlorides, and boron, to pass. As a result, the run time of the media beds is extended and the volume of media to be disposed is reduced.

These selective media last longer than conventional organic ion exchangers, as a larger fraction of their exchange capacity is used to remove the targeted radioisotope, instead of removal of innocuous species. Likewise, selective media benefit from higher decontamination factors, which is important when striving to

reduce 100,000 Bq/L (3 E-3 μ Ci/ml) of radioisotope contamination to <2 Bq/L (5 E-8 μ Ci/ml).

The full-scale SIEX System consists of eight columns, loaded with selective media based on the isotope targeted, and operated sequentially. The three principle selective exchangers for concentrate cleanup are:

- Cs Selective
- Sb Selective
- Co/Mn Selective

The limits being imposed by new legislation will reduce the permissible level for some isotopes and lower levels due to the summation of all isotopes. To meet these very stringent new limits, additional columns of selective ion exchange media will be required to remove some of the isotopes that were not expected to be of concern in the past. These isotopes include selenium (Se), Ag, Mn, arsenic (As), cerium (Ce), and zirconium (Zr). This also means that C-14 and H-3 add together in the summation so that the fraction of the limits for all isotopes must equal <1. Although the overall consumption of SIEX is not expected to increase, the need to remove the additional isotopes means media must be selected that will remove these isotopes.

Typically, the Cs selective media is loaded into Vessel 1; additional Cs selective media is loaded into Vessels 2 and 3; the Sb selective media is loaded into Vessels 5 and 6; and Vessel 7 is utilized for media effective for Co and Mn. Vessel 4 will be held for future use with the media to be determined depending upon isotope loading. Vessel 8 is often utilized for polishing using highly selective media for Cs and Sb.

When the first of the columns of either media becomes completely exhausted, or the last vessel of that media begins to break-through and leak the targeted isotope, the first column is sluiced out and new media loaded. The SIEX design provides a simple means of altering the vessel sequence, such as the first vessel that was sluiced out and loaded with fresh media can be valved in as the last of that media, or polishing, vessel in the sequence of two or three vessels used to apply that particular selective exchanger.

For instance, the initial line for the Cs vessels would be 1-2-3. When the first vessel is depleted, sluiced out, and reloaded with new media, the sequence would be changed to 2-3-1. This positions the new media at the end of the sequence of vessels applying that particular media.

In this polishing position, the fresh media has the ability to produce the highest quality water. At the same time, the older bed, which has been moved to the front of the sequence, will continue in service, loading the media bed to the maximum capacity. This lead-lag logic scheme is utilized in all of AVANTech's liquid radwaste (LRW) processing systems and is very successful in minimizing waste volumes, while maximizing process stream decontamination.

Thin Film Evaporator/Mixer Dryer

The Mixer Dryer is essentially a two-part evaporator that, instead of generating a liquid concentrate, produces a dried granular solid into the drums. The first part is a Thin Film Evaporator (TFE) that rapidly further evaporates the concentrate causing it to begin precipitation. The resultant sludge is then transferred directly to the attached Mixer Dryer. Both utilize hot oil to heat the TFE and Mixer Dryer via jacket and screws. The rate of evaporation is increased by application of a vacuum to the dryers, effectively lowering the boiling point of the liquid. The discharge of the Mixer Dryer maintains the vacuum while dropping solids to the drum.

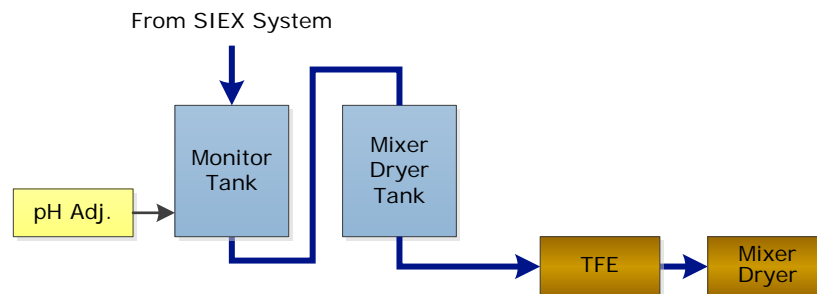


Fig. 6. TFE/Mixer Dryer Concentrate System
Final Product: Dried Granular Solids / Clean Distillate

By calculation, it was determined that if the feed water to the TFE/Mixer Dryer from the SIEX is <5 Bq/L, the dried solids will be sufficiently low in Becquerel concentration that the drums of solid material, consisting principally of crystallized boron, will meet the limit for free-release for recycle or disposal as industrial waste, while the distillates can be free-released to the environment.

A key aspect of the Mixer Dryer operation is the use of AVANTech's patented treatment process[1], which converts the high boric acid containing material into a granular free-flowing solid and removes CO₂ containing C-14 and water containing H-3. This has the effect of allowing the drum to be filled to a very high level and permits a high rate of continuous distillate production.

The TFE/Mixer Dryer control skid controls the application of heat and vacuum to keep both in the safe, optimal range. The liquid vapor is re-condensed to liquid in the condenser system for return to the plant, or as an alternative, the water vapor can be allowed to be removed through the exhaust system. The TFE/Mixer Dryer control skid, in addition to controlling heat and vacuum, provides for automated feed control of the concentrate to the TFE.

The control skid's programmable logic controller (PLC) records operating data and initiates visual and audible alarms, controls safety interlocks, and secures the unit to a safe shutdown mode if any set parameter is exceeded.

If C-14 is to be removed, the pH of the concentrate must be lowered to pH 4 to be able to assure conversion of 100% of the carbonate to CO₂. The CO₂ is then

removed with the water vapor and is assisted by the application of a vacuum that also lowers the boiling point of the water and the vapor pressure of the CO₂, thus increasing heat transfer efficiency and vapor removal. The combination removes >99.99% of the CO₂, lowering the C-14 in the water by more than three orders of magnitude and decreasing the C-14 to acceptable and normally undetectable levels. H-3 is also removed with the water as there are no waters of hydration for boric acid.

The Mixer Dryer is able to operate under acid conditions, enabling the simultaneous removal of both C-14 and H-3 at the normal boiling point of water. This eliminates the need for repeated pH adjustment, which reduces chemical usage and power consumption.

CONCLUSIONS

The CTS™ provides a versatile and cost effective approach to reducing the quantity of radwaste that is generated from nuclear plants, minimizes activity to the environment, and provides a product that can be utilized for recycle to non-nuclear industries which could provide some revenue rather than burial cost. Even if the byproduct has no industrial reuse, the solids can be disposed at industrial disposal sites with a tiny fraction of the cost of radwaste.

The whole process has been successfully demonstrated on actual concentrates from Bohunice and Mochovce Nuclear Power Plants in Slovakia to meet IAEA limits. This process will be demonstrated again in Germany using actual concentrate at a PWR. The full-scale equipment is currently under fabrication and will be installed and demonstrated later this year at Mochovce. The equipment for Bohunice will be installed approximately a year later.

REFERENCES

1. D. Brunzell, C. Jensen, and L. Beets, "Concentrate Treatment System." U.S. 2015/0221404 A1.

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