

CONCEPTUAL DESIGN OF A MULTIPURPOSE EFFLUENT PROCESSING FACILITY

M.-F. Debreuille
COGEMA*

N. Hubert, J.-P. Moulin
SGN**

G. Stegen
COGEMA Eng***

ABSTRACT

Vitrification is widely recognized as the best nuclear waste packaging. Nevertheless, liquid waste must be submitted to a pretreatment prior to a vitrification. For acidic non salt bearing nuclear waste, this pretreatment can be limited to plain concentration by evaporation. With alkaline or salt bearing waste, the problem is more complicated and the pretreatment to be applied depends upon the chemical and the radiochemical composition of the waste. The paper discusses the selection of chemical process and process technologies to perform the most cost-effective pretreatment of this liquid waste.

PRETREATMENT OF RADIOACTIVE EFFLUENT WITH HIGH NON-RADIOACTIVE SALT CONTENT

Vitrification is universally recognized as the most effective technique for immobilizing high-level radioactive waste. It provides a durable waste form with relatively low final volume because volatile components are driven off and the glass matrix is able to accommodate a relatively high content (20 to 50 wt%) of the residual waste oxides.

In most cases the radioactive waste transferred to the vitrification process requires some kind of pretreatment to result in an economical process. In the COGEMA reprocessing plants, the high level waste raffinates consist primarily of nitric acid and water plus fission products and transuranics. For this case, the needed pretreatment is limited to concentration by evaporation. Other types of waste exhibit very different characteristics, such as the presence of significant amounts of sodium salts. Direct vitrification of such waste may result in production of an excessively large volume of glass. In many cases it is found to be more cost effective to separate out sodium salts and other non-radioactive components prior to vitrification. This results in a much smaller volume of immobilized radioactive waste, and also a smaller vitrification process.

Liquid wastes that may benefit from separation prior to immobilization include :

- Low-level waste from facility operation, maintenance, equipment decontamination, laboratories, and miscellaneous sources. These frequently have high content of non radioactive salts and other components.

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- Effluent generated from decommissioning of shutdown facilities. Examples include the oldest reprocessing plant in France-UP1 at Marcoule, which has been closed since 1997 and the planned decommissioning of the oldest UP2 facilities at La Hague.
- Supernatants of neutralized defense wastes at Department of Energy sites in the United States.

Cesium and strontium are often dominant fission products that drive selection of the preferred separations approach. Transition metals such as ruthenium and technetium, actinides, and even semi-metals such as antimony may also be of importance. Because of the complex chemistries involved, it is not always possible to find a single reagent or chemical process capable of separating elements with such different chemical properties. Selection of the preferred separations approach must also consider radioactivity of the solutions, especially gamma emitters. Many years of operating experience at the La Hague reprocessing plant have successfully demonstrated the ability to process highly active solutions on a production basis ([1], [2]). However, the cost of the necessary remote cells and equipment is high, and it may therefore be advantageous to remove significant gamma emitters at the head end to reduce radiation levels in downstream process steps. The following sections discuss separation technologies commonly encountered in radioactive liquid waste treatment, and an example process concept developed for treatment of wastes from the Marcoule plant.

CHEMICAL PROCESSES FOR SEPARATING RADIONUCLIDES AND SODIUM

Cesium

Separating cesium from sodium (and from potassium) on an industrial scale is a major challenge. These elements have only one oxidation state (+1) in solution and are little affected by sequestering. Since they have similar chemical properties, they are difficult to separate and—in practice—only chemical property variations related to their different steric hindrances allow them to be separated.

- Ion Exchange
 - * Natural mineral exchangers such as the zeolites have partition coefficients that favor cesium extraction in saline and alkaline media. Many other synthetic exchangers have been developed [3]. Both natural and synthetic products are sensitive to the sodium content of the solution to be treated (see Figure 1). In practice, only high-performance synthetic products can be used with the most concentrated solutions to avoid generating prohibitive glass volumes, even if their mainly silica-based substrate is favorable for their vitrification.

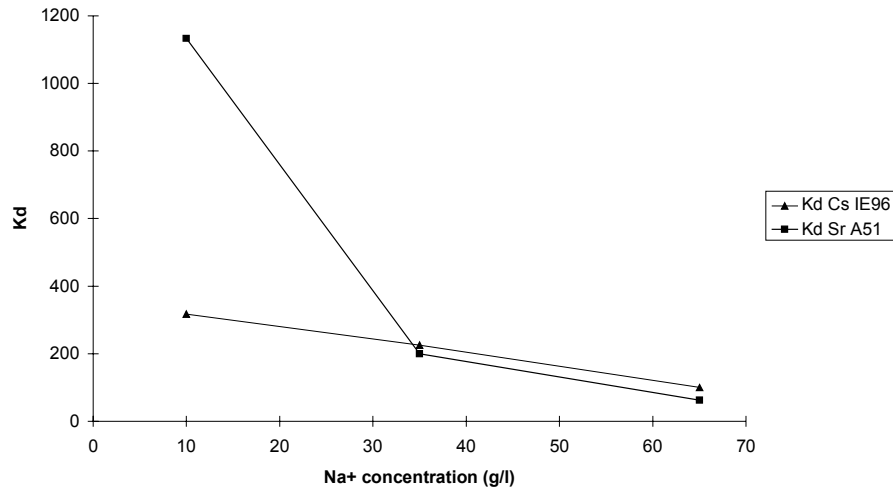


Figure 1 : examples of strontium and cesium Kd for zeolites

- * Various organic ion exchange resins, such as the resorcinols, offer high selectivities for the sodium, which is not extracted, and for the cesium, which is removed [4]. At least in theory, these resins can be relieved of their cesium by elution and therefore recycled.
- * Various ferrocyanides of nickel, cobalt, potassium and other elements show extremely high affinities for cesium and are relatively insensitive to sodium content ([5], mentioned in [6]). They are, however, limited with regard to the usable pH range because they decompose at the most alkaline pH levels. The potassium content of the treated solutions also affects their efficiency. The redox properties [3] of these compounds give reasonable hope of being able to elute their cesium because, even if they can be incorporated in glass, they pose two problems: the incorporation of large quantities of iron in the glass and the destruction of the cyanides, which has to be closely controlled.
- Precipitation
There are substantial differences in solubility between the sodium salts (soluble) and the cesium salts (very low solubility) of certain polyanion salts such as cesium tetraphenylborate, which is insoluble even at the highest pH levels.
- Sequestering
This promising technique is being investigated in several laboratories for highly selective sequestering of cesium using specially synthesized molecules, the calixarenes. Use of these molecules, which are expensive, is conceivable, for example in liquid-liquid extraction, but would involve considerable difficulties. Although these difficulties could surely be overcome, they make industrial use of the molecules unlikely in the near future.

Strontium

Strontium is an alkaline-earth metal. Its chemical properties suggest a number of separation methods.

- **Precipitation**
Strontium sulfates and carbonates are insoluble and both avenues have been investigated. Although precipitation of the sulfates is easier, the need for a carrier requires relatively large quantities of sulfate whose presence is not desirable during vitrification. Precipitation of the carbonates imposes relatively stringent pH adjustment conditions and reagent concentrations.
- **Ion exchange** can be used to separate strontium. Usually mineral exchangers, zeolites and monosodium titanate (MST), have been proposed and tested. This leads to difficulties on a level with those encountered for the separation of cesium.
- As for cesium, techniques have been investigated that should eventually enable liquid-liquid extraction. Strontium may be sequestered selectively by certain crown ethers. Use of these molecules, which are expensive, is at a slightly more advanced stage than that of the calixarenes. Nevertheless the incentive to develop this process is less than for calixarenes as the other strontium separation techniques have specific qualities, particularly in terms of cost.

Transuranic Elements

Although the neutral hydroxides of the transuranic elements ($\text{Pu}(\text{OH})_4$, $\text{Am}(\text{OH})_3$, etc.) are highly insoluble, the effluent may contain transuranics that are soluble because they have been sequestered by anions that solubilize them (carbonates, DTPA, etc.). In the absence of sequestering agents, very high decontamination factors can be achieved by precipitating these hydroxides and entraining them through ferric hydroxide, which requires meeting fairly stringent pH conditions (optimal at pH 10). The presence of certain sequestering agents considerably reduces these decontamination factors, unless the agents are destroyed or masked.

Some mineral exchangers, e.g. the titanates, extract the transuranic elements to a significant extent and may contribute to decontamination.

Other Metals

These metals include the lanthanides, ruthenium and technetium. Although the lanthanides behave like the actinides in most separations, the others are more problematic. Ruthenium separation is seldom very effective due to the extreme chemical complexity of this element. Ruthenium has been coprecipitated in sulfide form with cobalt sulfide in COGEMA's effluent treatment facilities, as well as with ferrous iron/cupric copper. Ion exchange and electrochemical separation methods [3] have been proposed for technetium.

SEPARATION TECHNOLOGIES

Precipitation

The processes normally used to chemically separate the radionuclides rely on precipitation or ion exchange conducted under conditions similar to those of precipitation, i.e. in vessels. Use of these operations in batch mode is not ideal for handling high effluent flowrates. A stirred tank reactor (CSTR) meets the flowrate and efficiency requirements and enables sequencing several operations through a cascade of reactors.

Ion Exchange

Ion exchange may be used in a number of ways, such as through simple contact in a cascade of stirred vessels (as in the STE 3 facility at La Hague), which ends with a solid-liquid separation like those reviewed above, or in stationary phase or moving bed chromatographic columns ([7] and Figure 2). In their principle, the columns are much more effective in terms of the decontamination achieved relative to the quantity of sorbent used.

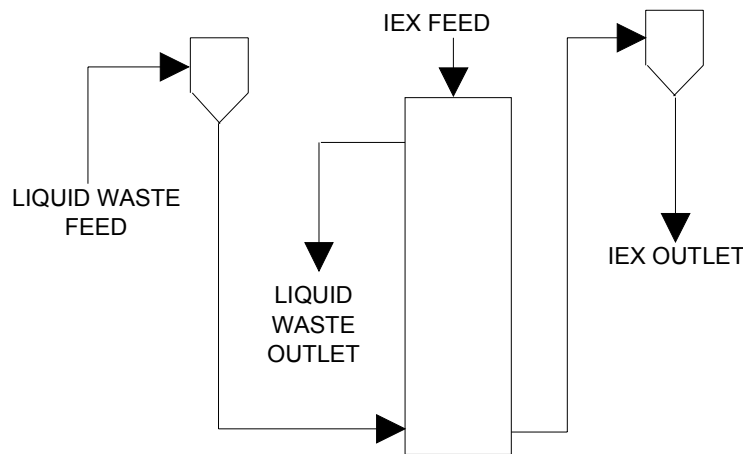


Figure 2 : sliding bed chromatographic column

It should, however, always be kept in mind that nuclear phenomena practically require confining operation of the chromatographic columns to low and medium activity levels. This is because the buildup of large quantities of radioactive cesium in a resin or high-performance mineral exchanger column will cause radiolysis and release thermal energy incompatible with acceptable use. Cooling of such a column is therefore mandatory, which makes it a safety-related function that must be ensured even in the event of a failure. If the column has a large diameter, in addition to conventional channeling risks, the highly limited thermal conduction in the dense bed will create a temperature profile with a maximum at the column center. If the temperature difference exceeds around 50 degrees, operation of the column will be subject to serious disturbances that could even prevent its use. The radiolysis will generate gases and, if the release is substantial enough, will form bubbles that will disturb flows and prevent proper operation of the column (with organic resins). In any event, even with mineral exchangers, radiolysis will

release hydrogen that will have to be controlled and suitably diluted to maintain the safety of the facility.

These examples, which are not exhaustive, show that chromatography and—more generally—the techniques using dense beds of particles heavily laden with high-level radionuclides, involve difficulties that clearly may not be overcome at an acceptable cost. The decisive advantage of loose particle beds in this respect indicates that the use of ion, mineral or organic exchangers for high activity effluent should be oriented toward combinations of contacts in loose beds. This is preferable to dense bed operation, which—as shown above—is not very realistic.

Solid-liquid Separation

Many chemical separation processes produce precipitates or use fractionated solids that have to be separated from the solution they helped to decontaminate. Numerous technologies can efficiently perform solid-liquid separation of the pulps.

- **Settling**

In the most favorable cases, settling can be used by itself. This is particularly the case for the STE 3 effluent treatment facility at COGEMA's La Hague plant, where the precipitation solutions are settled prior to filtration. When the precipitation is accompanied by flocculation, either spontaneous or due to addition of a flocculating agent, settling is often the most appropriate method because the flocs—particularly the spontaneous ones—are especially sensitive to shearing forces, which are clearly absent when this technique is used, unlike for centrifuge separation or even ultrafiltration. The decontamination factors achieved with settling alone are, however, limited due to the presence of fines that cannot be settled out. The process is therefore generally restricted to a pre-separation stage.

- **Front-end Filtration**

This highly conventional technique used in non-nuclear industries exists in too many variations to be reviewed here. Nuclearization constraints, particularly in high-level environments, restrict the range of possibilities. Effluent that is not heavily laden may be filtered through batch units, whose nuclearization presents no particular difficulties. The more heavily laden pulps are filtered in continuous units, which may be used in the nuclear industry. A layer of diatomaceous silica or other filter aids is often used to protect the filter from fouling. COGEMA uses this type of filter in several facilities, e.g. the STEL effluent treatment facility at Marcoule, where a rotary drum filter is operated, in compliance with nuclearization requirements (motors installed outside cells, etc.). COGEMA uses other continuous filters in facilities that are not dedicated to effluent treatment, such as facilities for conversion of plutonium into oxide (T4, R4 and MAPu facilities at La Hague) in the stage for separating plutonium oxalate from its mother liquors ([8], [9]). This separation is performed using a rotary drum filter.

- **Cross-flow Filtration**

The advantage of this technique is that it can be applied to fouling pulps. In addition, after activity concentration, operation in diafiltration mode (at constant volume) can clean the

residue to further reduce the quantity of sodium and other troublesome soluble ions. COGEMA uses an ultrafiltration separation to treat the analytical effluent in the central building of the UP3 plant at La Hague. This high-performance unit, which achieves a Pu decontamination factor of more than 10,000 [10], separates the actinides from a medium rich in exotic ions and sequestering agents by coprecipitation with ferric hydroxide. The nuclearization of ultrafiltration, which is a highly attractive technique, involves difficulties in high-level environments due to recirculation pump selection and to the presence of a fluid at a higher pressure than that in the cell, which requires particular attention to seals and especially to their maintenance during replacement of the membranes. COGEMA has overcome these difficulties at the La Hague plant. Specifically, this application led to the development of a nuclearized ultrafiltration unit that can be refurbished in compliance with all high-level effluent containment principles (see Figure 3).

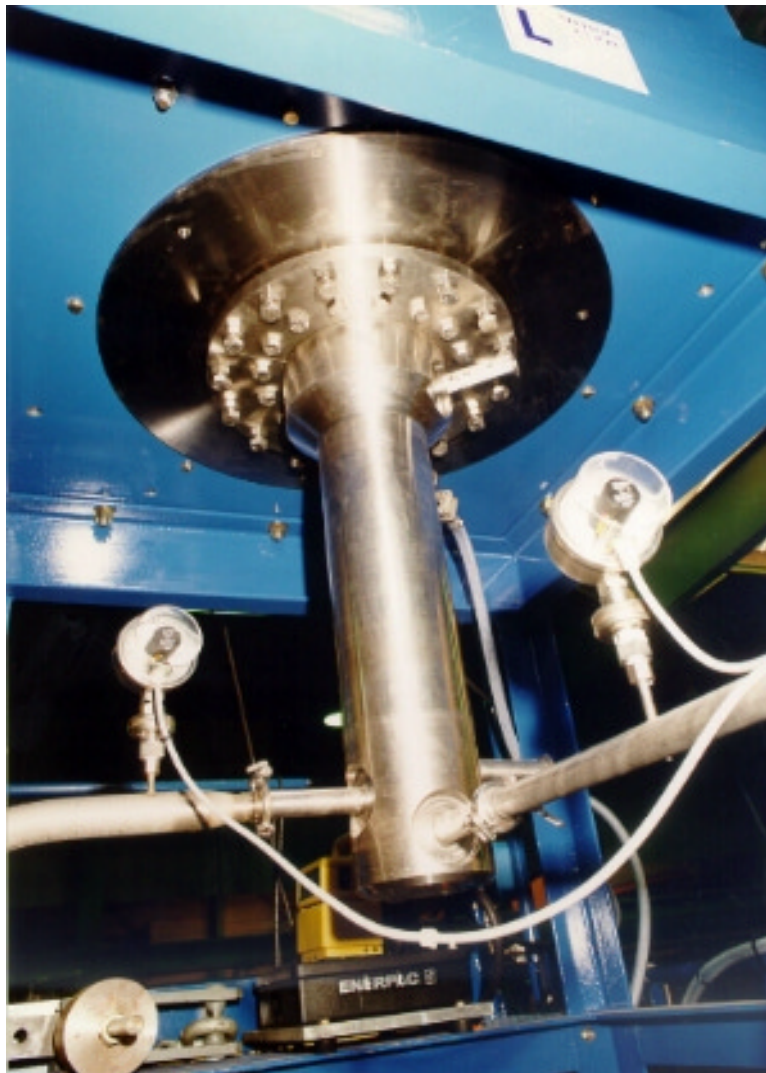


Figure 3 : COGEMA's nuclearized ultrafiltration unit

- **Centrifuge Separation**

This high-capacity technique, which is well suited to treating low density pulps, uses sophisticated high-speed rotating mechanical equipment whose nuclearization may seem very difficult. COGEMA has expertise in this technology for high-level environments with DPC 900 centrifuges that have been operated for more than nine years at the UP3 plant (five years at UP2-800) to separate dissolution fines from the nuclear fuel dissolution liquors, which are very high-level media. No significant incident has been reported during this period. However, provision has been made for replacing the centrifuges and the operation was performed once at UP2-400 on the previous model, the DPC 800. This technology may therefore be used for any activity level with a solid guarantee of performance and durability.

Liquid-liquid Extraction

This technique, which is recognized as well suited to all activity levels, is too well known to the nuclear community to discuss its efficiency here. It can be used with three major types of technology: mixers-settlers, centrifuge extractors and pulsed columns. The chemical separation operations it may use have not reached industrial maturity. It should also be recalled that a liquid-liquid extraction facility requires numerous process annexes that make it expensive—significantly more so, for example, than for separation facilities using precipitation and filtration.

Separation by Electrochemical Deposit

Several proposals have been made to decontaminate effluent by depositing an insoluble radionuclide compound on an electrode. This technique is particularly attractive because it does not introduce any reagent into the solution, and because it is relatively easy to clean the electrode by periodically redissolving the deposit. No treatment of nuclear effluent of significant activity is known to use this technology. However, it clearly could be used because COGEMA has commissioned a unit at La Hague to recover silver from the waste of a plutonium dissolution. This dissolution is performed by using AgII electrogenerated. Therefore sending silver to vitrification, which can accommodate only very limited quantities, is limited.

CONDITIONING SELECTION CRITERIA

Nuclear waste conditioning matrixes are required to meet quality criteria to ensure long-term containment of the material they encapsulate. These criteria are formalized by specific national regulations and concern particularly the material's resistance to leaching of water that could come in contact with packages during storage. The characteristics of the conditioned radionuclides, the quantities included in the packages and the storage conditions are considered when determining these criteria.

The quantity of material that can be incorporated in a specific volume of final waste is taken into account when selecting the conditioning matrix. For a specified matrix, this quantity depends on the nature of the elements that compose the waste. The presence of inactive salts in the highly saline effluent is normally unfavorable for obtaining a high encapsulation ratio, unless the salts are a component in the structure of the conditioning matrix.

For the conditioning of waste from the treatment of differing types of effluent, the variations in the composition of the initial effluent—hence of the waste to be conditioned—also strongly limits the encapsulation ratios. This is due to the need to ensure compliance with the aforementioned quality criteria for a composition range tested upstream of the production of the actual packages, and to the known sensitivity of certain matrixes to specific chemical elements, e.g. the solubility limit of sulfate in the borosilicate glass.

In this respect, some packages will be more suited to accommodating composition variations than others, both because of the selected incorporation matrix and the specified quality criteria, particularly when the emitters to be incorporated have short or medium half-lives. This limits their storage period to around 300 years, making it possible to take into account repository surveillance guarantees that cannot be envisioned for waste containing long-lived emitters.

Although the nuclear material containment qualities of the glass matrix have been demonstrated, the glass imposes fairly stringent requirements for the composition of the effluent to be incorporated, in order to ensure the required quality. Separate phases may be formed for certain non-digested elements and it will therefore be restrictive for treatment operations which, while separating the radionuclides from the sodium, add other chemical elements, e.g. titanium for the separation of the transuranics or strontium. As a result, glass is preferably reserved for the radionuclides whose half-life requires a higher conditioning quality and for the solutions that can be concentrated in radionuclides without concentrating the associated chemical elements in the initial effluent, unless a lower quality glass suited to high flowrates is developed for specific flow requirements.

Bituminous and concrete matrixes are more flexible with regard to the chemical composition of the encapsulated solutions. They are therefore used in many medium- or low-level effluent treatment facilities to process effluent with a wide range of characteristics.

A CASE STUDY: THE LIQUID EFFLUENT TREATMENT FACILITY AT MARCOULE

Radioactive sodium bearing liquid waste is generated by the degreasing rinsing performed during decontamination operations at the UP1 reprocessing plant at Marcoule, France. This waste cannot be incorporated in the high-level borosilicate glass produced in the existing AVM vitrification process without producing a very large number of packages of glass. The glass quantity is determined almost directly by the quantity of sodium in the waste. This waste is therefore transferred to the STEL treatment facility, which separates and concentrates the radionuclides through a series of coprecipitation steps followed by filtration. The treated waste is immobilized by incorporation into a bituminous matrix. Coprecipitation sludge from the STEL process is not compatible with vitrification because of the chemicals present, especially barium sulfate that is used for strontium decontamination. Engineering studies and testing were performed to identify alternative process approaches using separations and vitrification that could significantly reduce the volume of the resulting immobilized solid waste product. The resulting optimized process includes the following features (figure 4):

- Coprecipitation with ferric and cupric hydroxides to separate the transuranics and ruthenium, followed by solid liquid separation and treatment in columns to separate strontium and cesium. The separations are performed in several stages to optimize conditions and thereby limit required additive reagent quantities.
- Use of an improved ultrafiltration technology. This allowed most of the soluble sodium to be purged from the waste in a very low activity liquid waste stream that is suitable for discharge.
- Use of ferrocyanide is reduced by use of sliding bed ion exchange technology [7].
- Use of titanate in columns for strontium removal.
- Vitrification of the resulting sludges and ion exchange media in the existing AVM vitrification process at Marcoule.

The estimated highly active waste would have been drastically reduced as compared with bitumen immobilization. Anyway, the Marcoule site already has a high-performance bituminization unit and has already produced a large quantity of bituminized waste. As the D&D bitumen production represents only a small fraction of it, the decision was made to rely both on vitrification and bituminization for D&D waste.

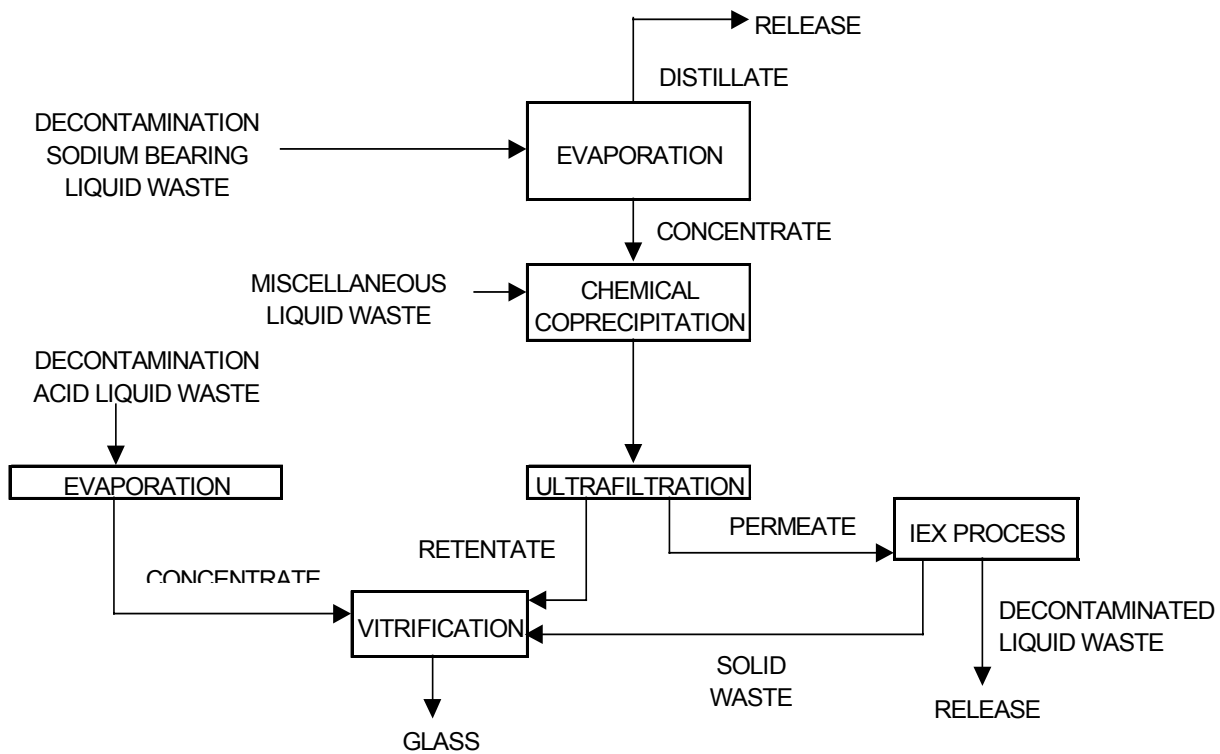


Figure 4 : liquid waste treatment facility concept

CONCLUSION

There is no universal treatment for radioactive effluent, particularly when it has a high salt content since mere concentration cannot be used as pretreatment: incorporation in a matrix would either generate waste quantities considered too high or waste of inadequate quality. With the selection criteria mentioned above, however, it is possible to design a given facility with an effluent treatment that optimizes total treatment/conditioning cost and the quality required for the waste products, while accommodating effluent composition variations.

The principles used are to separate the decontamination operations according to:

- The desired decontamination factor. When a very high factor is required, it is often highly advantageous to split the operations into several stages
 - * to be able to use, for the low or medium activity levels, technologies whose application in high-level environments is neither realistic nor beneficial due to maintenance requirements,
 - * to limit the size of required high-level facilities, which will be installed in special cells with adequate remote maintenance,
 - * and to avoid recycling solutions that pollute the least active effluent due to the residual contamination of the facilities, lower efficiency and increase the volume of the high-level facilities due to the required oversizing.
- The characteristics of the radionuclides. To obtain the required overall process efficiency while keeping capital-cost as low as possible, it is necessary to pay attention to the following:
 - * Selecting the fittest process to decontaminate a radionuclide with allowance for the other elements to be decontaminated,
 - * Combining decontamination functions according to their half-lives to optimize waste generation by category,
 - * Combining decontamination functions according to the nature of the chemical reagents. This may require splitting the treatment into several stages divided up by solid-liquid separations.

COGEMA has extensive experience in the industrial development of nuclear processes that offer a high degree of flexibility. As a result, the radioactive effluent treatment concepts described may be applied to optimize waste generation with high-quality glass, low-level waste and very low-level decontaminated liquid.

FOOTNOTES

* COGEMA 2 rue Paul Dautier BP 4 78141 Vélizy Villacoublay Cedex, France

** SGN 1 rue des Hérons Montigny le Bretonneux 78182 St. Quentin en Yvelines Cedex, France

*** COGEMA Engineering Corp. P. O. Box 840, 2425 Stevens Center, Richland, WA 99352, USA

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