1. Introduction

The operations involved in the treatment of a low- or medium-level liquid radwaste generated at a nuclear plant include:

- concentration of the radioactivity present into a minimum volume for conditioning and subsequent disposal; and
- the ability to release most of the aqueous phase into the environment after decontamination.

This problem is faced by all the actors in the nuclear fuel cycle, and it is important because it concerns significant volumes.

With the backing of its parent company COGEMA, of CEA, the French Atomic Energy Commission and benefiting from assistance contracts with ANDRA and cooperation agreements with EDF, SGN has built up considerable know-how and enjoys thirty years of feedback in the industrial management of liquid effluents from the entire French nuclear industry, expertise which it offered very early to its foreign clients.

SGN has accordingly completed the engineering and commissioning of many LL/ML radwaste treatment facilities, relying on two major industrially proven technologies; evaporation and chemical coprecipitation.

These units have always been integrated within a concept aiming at the minimization of effluent production at the source, careful segregation of waste, and good engineering of the collection, storage, and sampling systems, intended for the optimum integration of all the links in the treatment chain up to final disposal.

2. Evaluation of LL and ML Radwaste

Evaporation is the process by which a solution is concentrated through the removal of a volatile phase by the action of heat.

The liquid radwaste is evaporated to form a small stream containing all the non-volatile components at the column bottom, and a head stream composed mainly of steam, which is condensed, other volatile compounds, and traces of entrained initial compounds.

Liquid radwaste evaporation is the most widespread form of treatment in reprocessing plants, nuclear power plants, and research centres. Combined with an effective steam purification technique, it helps to obtain very high decontamination factors (DF) for nearly all the radionuclides present, and generally makes it possible to discharge the distillates obtained directly into the environment.

SGN, which has built up considerable industrial experience in this technology, that it has been
used extensively for delicate evaporation and distillation operations at the very core of the process applied in reprocessing plants, enjoys complete industrial expertise in evaporators featuring external boilers and natural circulation (thermosyphon evaporators). The simultaneous application of this technology to non-nuclear uses on industrial wastes, where especially difficult problems of foaming and crust formation are encountered, and where the economic factors are extremely important, have enabled SGN to extend its know-how and references to other types of evaporator, better suited to the concentration of LL/ML liquid radwaste, namely:
- “pot” type evaporators, with double jacket or submerged tube bundle, and
- external boiler evaporators operating with forced circulation.

The number of possibilities offered by the various types of evaporator is further enlarged by the choice of the boiler heating mode. Depending on the conditions and the place of operation, and depending on the capacity, it may be preferable to select a process with thermocompression or mechanical recompression of the steam produced by the evaporator, recycled as a heating fluid.

Based on this experience, SGN has developed an optimized evaporation system to treat low- and medium-level liquid radwaste commonly found on reactor sites and in nuclear research centres. The system offers outstanding decontamination performance (DF normally ranging from $10^6$ to $10^7$ for non-volatile species), excellent reliability, and easy operation.

A circulation pump can be used for this type of radwaste, and this has led to the proposal of forced circulation evaporation with submerged flash, offering several advantages:
- operating stability in a wide range of evaporation throughputs;
- high flow speed in the recirculation loop and the boiler, which helps to prevent the deposition of suspended matter on the heat exchange surfaces;
- boiling in the evaporation chamber where flash is developed, thus the absence of effluent evaporation and concentration in the boiler circuit prevents its scaling; and
- the “submerged flash” solution, combined with a suitable technology, helps to reduce droplet entrainment, generally very high in flash systems, to levels comparable to those found in conventional boilers.

The concentration factors obtained obviously depend on the initial salt content of the effluent and on the solubility of these salts. Yet values in the range of 10 to 100 can be obtained routinely. In the treatment of effluents containing sodium nitrate, for example, the concentrates obtained have a salt content as high as 750 g/l.

Evaporation can be performed after prior neutralization of the effluents or on acidic effluents. With acid effluents, evaporation helps to recover the acid and to avoid the storage and conditioning of substantial amounts of salts. Corrosion risks can be reduced by choosing “noble” materials, or by operating under partial vacuum at lower temperature, which significantly reduces the corrosion kinetics.

Note that the steam/liquid separation stage is obviously very important, because the distillate obtained after condensation must be as decontaminated as possible. A unit that promotes the separation of the steam and entrained droplets is an indispensable complement to the actual evaporator.

This is why SGN together with the CEA has conducted a Research and Development Program for the design, engineering, and industrial-scale development of steam purification systems, and the
means of combining these units to prevent the buildup of activity, to minimize maintenance problems, and to favor simplicity and decontamination factor stability within a broad flow range around the nominal throughput.

For steam purification, this program led to the combination of a scrubber equipped with Venturi trays, involving a new principle, and a parallel blades separator. The operating principle of the Venturi tray column is based on "liquid/gas" contact at each tray, by dispersion of the washing liquid in fine droplets into the gas to be purified. The steam flows at high speed through the mini-Venturis, replacing conventional bubble cap trays. This principle demands a very large specific surface area for contact, together with a high level of turbulence in the gas. This enhances transfers and ensures much higher efficiency, with a more compact column than in the conventional arrangement, in which the phases are placed in contact by simple bubbling of the gas through the wash liquid.

Tests conducted in identical conditions, on the same type of aerosol, with the same gas and wash liquid throughputs, showed that the decontamination factor of a Venturi tray is twice that of a bubble cap tray of the same size.

Experience has shown that, with a purification column equipped with a thermosyphon boiler, a column with three Venturi trays achieved a total decontamination factor over ten times that of a column with five bubble cap trays.

The parallel blades demister, developed by SGN for the purification of gases and vapors, runs on the principle of parallel blades settlers. In this unit, the gases entraining the liquid particles have a laminar flow at a speed of about 1 m/s between the parallel blades, which are spaced at intervals of a few mm.

90% efficiency can be obtained for 3 μm water droplets entrained in steam at atmospheric pressure. Settling is still effective for 2 μm particles. Side effects, such as Brownian diffusion, are also involved in the capture of smaller-diameter particles.

A first steam purification column has been installed on an evaporator of the Tricastin power plant. This type of tray has also been selected for the evaporators of the Sizewell B power plant in the United Kingdom.

Many industrial projects have resulted (design, construction, and commissioning) in response to the wide variety of client needs, either for the concentration of salt solutions (concentration of borated effluents in PWR power plants) or for purification considering the very high DF obtainable in order to meet increasingly stringent release standards.

The systems have since extended from low-capacity forced-circulation evaporators (about 250 l/h) to evaporators of the effluent treatment stations of PWR and BWR power plants, including larger-capacity evaporators (6 to 9 m³/h) used at the Marcoule STE facility, for example, or intended for the future Japanese Rokkasho Mura reprocessing plant.

3. Chemical Coprecipitation of LL and ML Radwaste

In this process, the radionuclides in the effluents to be treated are made insoluble by coprecipitation, absorption and ion exchange with precipitates of inactive chemical elements, by the introduction of carefully selected reagents and the adjustment of clearly-determined pH and redox potential conditions, followed by the separation of the precipitates formed in the liquid phase.
A chemical process is hence always combined with a separation technology to produce a purified aqueous phase and a solid phase rich in radionuclides, that will have to be conditioned for disposal.

The first processes developed in the 1960s by the CEA were very similar to conventional water treatment techniques. However, these processes soon proved to be inadequate in terms of CF and DF. On completion of a number of major R&D projects conducted by the CEA teams at Cadarache, specific treatments by α and β/γ emitting radionuclides were developed:

- **α emitters**
  At pH > 10.5, α emitters, like Pu-239 and Am-241, coprecipitate with hydroxides (especially ferric). DFs higher than 1,000 are obtained in the absence of solvent or chelant.

  This decontamination can be improved by the introduction of titanium sulfate.

- **Examples of β,γ emitters**
  - Strontium-90
    Coprecipitation with barium sulfate in basic medium at pH > 8.5.
    DF = 50 ~ 100.

  - But also precipitation of:
    - Ca or Fe phosphate at pH 12,
    - Ca carbonate at pH 10.5 to 11, and
    - Mn dioxide at pH > 11.

  - Cesium-137 and cesium-134
    Addition of preformed nickel ferrocyanide precipitate (PPFNi) at pH 8.5.
    DFs over 100 and even 1000 depend on the pH at the end of treatment.

Several radionuclides are normally present in the effluent, making it necessary to form different types of precipitate simultaneously. The optimal conditions for their formation (pH, stirring, and residence time) are unfortunately too often antagonistic, and SGN has developed industrially-commisioned units consisting of lines of stirred reactors in cascades, each operating with the best operating parameters.

This process has been used extensively by COGEMA to treat LL and ML effluents generated by its reprocessing plants, up to capacities of 100,000 m³/year for the STE3 facility (17 m³/h continuously).

SGN has accordingly benefited from many industrial references for large-capacity installations such as STEL at Marcoule and STE2 at La Hague, which has been operating continuously since its commissioning in 1966, and has processed 710,000 m³ of liquid waste in accordance with the following average performance observed:

- DF total β/γ 20 to 50
- DF total α > 1000
- DF Ru 5 to 50
- DF Cs > 100
- DF Sr 50
- Concentration factors between 30 and 60.

The large volumes to be treated have led to the selection and development of continuous
processes, operated successfully thanks to the development, simultaneously with the
development of the chemical processes themselves, of original technologies concerning the supply
of active effluents at controlled flow rates without any mechanical equipment requiring
maintenance, continuous pH and redox potential adjustments, and reagents introduction at
controlled flow rates, with all these functions covered by central remote control in a nuclear
environment, where the effluents contain not only β/γ, but also α radionuclides.

The latest installation, STE3, was designed and built by SGN for COGEMA and has been
treating LL and ML effluents from La Hague since December 1987, particularly from the UP3
and UP2 800 plants, with the STE2 facility mentioned above only used to treat “suspect”
effluents.

Improvements to the chemical process applied, COGEMA’s determination to optimize waste
management and effluent segregation in the generating facilities, and the general policy for the
new facilities of increasingly sending the effluents after in-situ concentration to the vitrification
facilities, have led to treat volumes much smaller than the initial design capacity, namely,
55,000 m³ of LL/ML effluents in 1991, and especially to a substantial reduction of liquid
releases, for example,

• 8250 Ci β/γ in 1990 and 3130 Ci β/γ in 1991, and
• 7 Ci α in 1990 and 4 Ci α in 1991.

The choice of a chemical treatment process was justified by the appropriateness of these processes
for the treatment of effluents containing salts, the “stable” properties obviating the need to have
to make frequent adjustments in reagent types and flow rates. In addition, the rather modest
overall performance (DF = 10² to 10³ and CF < 10²) remained compatible with the release
standards in force at the time for French reprocessing plants.

For other operators besides COGEMA, this process was used for very specific applications in
which the effluent properties made them unsuitable for evaporation, for example if they
incurred foaming or fouling risks, or with treatment by ion exchange due to the saturation of the
sites by the inactive salts present. Laundry effluents containing detergents, and decontamination
effluents, are treated in this way.

In the final step, to facilitate settling and/or separation of the precipitates formed and containing
the activity, it is necessary to flocculate them.

Flocculation is designed to neutralize the electrokinetic potential or zeta potential of the particles,
either by the formation of hydroxides (ferric or aluminium) or by the addition of organic
polyelectrolytes. Slow stirring is necessary to avoid breaking the flocs formed.

Liquid/solid separation generally takes place by static settling of the sludges followed by final
clarification of the supernatants, but techniques such as centrifuging and filtration are also fully
within the scope of SGN.

Note that SGN, together with the CEA, also has development programs under way on
innovative techniques such as ultrafiltration, which makes it possible to achieve very high
separation efficiencies for the precipitates formed, thanks to the low porosities of the membranes
used, and also ensuring high concentration factors. A wide range of materials is available today
for the membranes, including inorganic materials that are perfectly suitable for use in the
treatment of LL and ML effluents.