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THE ORGANIC WASTE TREATMENT IN UP3-LA HAGUE

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ABSTRACT

The management of the solvent in the reprocessing plants has always been a difficult problem. Various process reasons lead to discard some contaminated solvent: this spent solvent is an organic waste the volume of which must be minimized.

To solve this problem for the UP3 plant, it has been decided to implement a distillation facility in order to split this spent solvent into three parts: recovered diluent and concentrated TBP, to be recycled in the extraction process, and a residue which contain the radioactivity and most of the impurities.

As the TBP is not highly volatile and as it is a thermosensitive compound, this distillation is performed at low pressure and temperature, with thin films evaporators, in order to minimize the residence times in heated zones.

The paper describes the selected process and the equipment employed. The R & D work which has been performed to define the process, size up the equipment and demonstrate the process is described, including the laboratory works, the pilot plant tests and the results of tests performed with a full scale prototype which has been built to demonstrate the whole process.

The industrial facility is described, and the results of the first active runs are described briefly.

INTRODUCTION

In nearly all reprocessing plants, the chemical purifications are performed by using the PUREX process. This process relies upon Liquid-Liquid extraction between nitric aqueous streams and solvent streams. This solvent is a mixture of an extractant, the Tri-nButyl Phosphate (TBP) and a diluent.

In French plants, the TBP content of this solvent is set to 30% per volume in a diluent which is a Hydrogenated Tetra-Propylene (TPH). The TPH is a mixture of a great number of hydrocarbons, the molecules of which contain a mean number of carbon atoms close to 12: it is often referred to as a "branched dodecane", even though its chemical properties are slightly different from these of the n-dodecane.

In reprocessing plants, the management of the solvent has always been an important topic:

- on the one hand, it is necessary to monitor the TBP content of the solvent continuously, and adjust it by adding pure TBP or diluent,
- on the other hand, the solvent must be washed from its degradation products.

For the plants put in operation before UP3, the solvent management relied on:

- alkaline washings for impurity removal,
- addition of fresh diluent or TBP to keep the TBP grade of the solvent at the set value. This, in turn, generates an excess of contaminated solvent.

Moreover an irreversible degradation of solvent is usually observed when a plant has been in operation for a long time. It is therefore necessary to periodically discard the whole solvent hold-up of, at least, the 1st uranium and plutonium purification cycles, producing then significant amounts of organic wastes, i.e. contaminated solvent.

From the very beginning of the design studies of UP3, it appeared that the systematic diluent washing of the aqueous streams leaving the extractors would lead to frequent TBP grade

adjustments of the solvent, and in turn, to the frequent withdrawal of contaminated solvent. As at the same time, the disposal of contaminated organics appeared to be a difficult problem, a decision was made to use a distillation process, in order to split the discharged solvent into three parts:

- a decontaminated diluent, to be recycled in the diluent washing of the extractions;
- a decontaminated solvent with a TBP grade far higher than 30%, for solvent adjustment purposes;
- a residue, which contains nearly all the radioactivity of the discharged solvent and the major part of the heavy molecular weight degradation products of the solvent; this residue is therefore the only organic waste produced by the solvent management. The outlines of the solvent and diluent management are shown on the figure 1. More details can be found in reference (1).

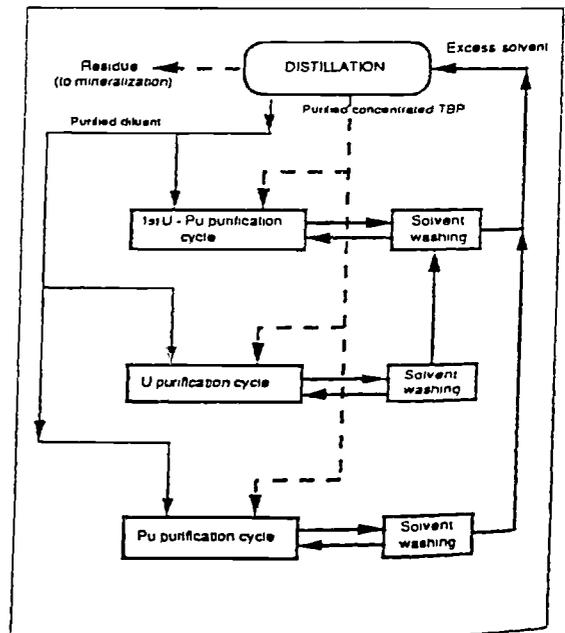


Figure 1 : Solvent Management

PRELIMINARY DEFINITION OF THE MAIN DISTILLATION PROCESS

The TBP is difficult to distillate:

- its molecular weight is quite high (0.266 kg/mol), and its volatility is accordingly low (its estimated boiling temperature is about 284°C at atmospheric pressure);

- moreover, the TBP poorly withstands high temperatures, and in such conditions, its decomposition is accelerated by the initial presence of degradation products such as Di-Butyl and Mono-Butyl Phosphoric Acids.

The diluent shows a straightforward behaviour, with a boiling temperature zone near 200°C at atmospheric pressure, and a robust thermal stability.

The conclusion was soon reached that the distillation had to be performed:

- at the lowest possible temperature, and therefore at the lowest achievable pressure, the selected pressure at the condenser is around 1 torr;

- with the smallest possible residence time.

Both choices aim at minimizing the thermal degradation of the solvent.

In order to fulfil the nuclear constraints, and particularly to limit the maintenance operations as much as possible, it has also been decided:

- first, to separate the residue (and therefore most of the radioactivity), by evaporating the diluent and the major part of the TBP together;

- to separate by rectification a

pure diluent, and a mixture enriched in TBP ($\geq 60\%$), but not pure TBP (which would be pointless);

- to withdraw the bottom and head fractions through a barometric seal;

- to use equipment without any moving part.

The selected equipment was:

- a thin film evaporator, where the process liquid stream and vapours flow co-currently downward for the solvent evaporation;

- a demister for decontaminating;

- a rectification tower fitted with a packing specially selected for its low pressure drop and high efficiency;

- a two step vacuum device, which includes a liquid ring pump and two stages of steam ejectors.

OTHER PROCESS EQUIPMENT

This process includes the following upstream steps:

- washing performed with acidulous water in a single mixer-settler stage, designed to wash any metallic salt which could be present in the solvent (or a significant amount of nitric acid);

- dehydration, the purpose of which is to prevent the major part of the water dissolved in the solvent, or entrained by it, from reaching the main distillation process (the presence of water is unwanted in the main distillation process, as it would behave as a non-condensable compound in the condenser of the main distillation process owing to the very low pressure, about 1 torr): this dehydration is performed under reduced pressure in a counter-current evaporator.

It also includes the following downstream operation: an alkaline washing of the recovered solvent, performed in a mixer-settler bank; its purpose is the elimination of the Di-Butyl Phosphoric acid which could be carried along by the TB₂P vapours.

RESEARCH & DEVELOPMENT WORKS

The Research and Development works devoted to this process were extensive. We summarize below the results gained, very briefly for the results already published (1) & (2) and going into more details for the latest results. The studies have been performed on three different scales:

- Basic studies, at laboratory scale, investigated:
 - the fundamentals of the solvent chemistry at temperatures higher than 100°C,
 - the results of runs performed with actual plant solvent in a mini-pilot plant (scale: about 1 /1000 of the industrial facility).
 - the properties of the recovered solvent and diluent which have shown that their physical and chemical properties (diluent flash point, solvent / aqueous phase settling times, ruthenium and plutonium retention) were very close to those of fresh solvent and diluent, and far better than those of routinely used plant solvent;
 - the cleaning of fouled surfaces of the tubes of the boiler. A procedure has been defined which allow to wash efficiently any fouling which may be produced by thermal degradation of the solvent processed.

- the phenomena of thermal striction which affects the wetting properties of a film of solvent when it flows under a thermal flux (3); these studies led to determine the minimum flowrate necessary for an efficient wetting of the heated area so as to prevent fouling.

-Small scale pilot plant (about 1/20 of the industrial facility). This pilot plant includes the dehydration step, the evaporation, the rectification and the alkaline washing of the recovered solvent. The main tests performed in this pilot-plant are the following:

- selecting and scaling the tubes of the full scale evaporator as well as sizing the rectification tower and dehydration evaporator;
- processing the solvent of a pulsed column rig which operates with uranium; from the beginning, many years ago, until now, no effect of the recycling of this solvent on the hydraulic behaviour and the extraction performances of the rig has ever been detected;
- a run has also been performed with actual UP2 plant solvent; this test has shown that the fission product Decontamination Factor (DF) was satisfactory on the recovered diluent and solvent; this recovered solvent has also been recycled successfully in the associated extraction rig;

-Full scale pilot plant. This pilot plant comprises all the operations of the industrial plant and for all significant parts, it uses the same technology as the industrial facility. The main results of this pilot plant are:

- . the demonstration of the feasibility of the process targets, i.e., dehydration of the solvent ($< 1 \text{ g.l}^{-1}$), residue rate ($\leq 5 \%$ of the feed), TBP content of the recovered diluent ($\leq 0.02\%$).

- . the study of the effects of the operating parameters on the DF, with different demister configurations in the vapour line;

- . the study of the effects of the operating parameters on the fouling of the evaporators, and the determination of a safe set of operating parameters (pressures, heating temperatures, flowrates, ...);
- . the study of the hydraulic behaviour of the mixer-settler bank devoted to washing the concentrated TBP, as its TBP content can be very high (up to 90%).

THE INDUSTRIAL FACILITY

The R&D results, and the engineering studies led to the definition of the industrial facility (see figure 2). The most salient features are the following:

- Dehydration: this operation is performed by counter-current evaporation at reduced pressure (about 37 torr); the operation is performed in a thin film evaporator, made of a set of vertical tubes. The distilled flow (water and a few diluent) are condensed and recycled to the mixer-settler upstream.

- Main evaporator: this equipment is basically a set of vertical tubes, heated by steam. The process liquid and vapours flow co-currently downward, and a recirculation of the residue has been provided in order to reach the flowrate necessary for a good wetting

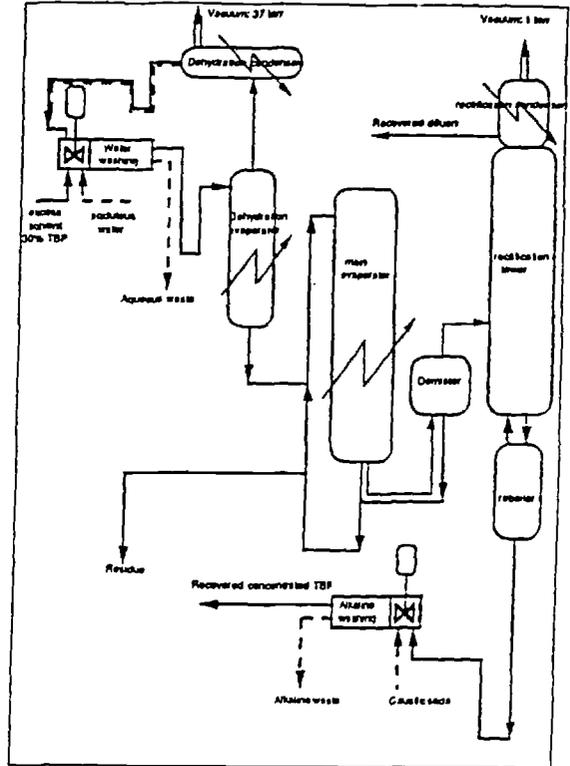


Figure 2 : Distillation flow-chart

and obtain therefore a very low residue rate, while avoiding any noticeable fouling. Nevertheless, as stated above, an efficient procedure for cleaning the tubes has been defined, and the relevant reagents inlets have been provided. The recirculation is performed by a set of two air-lifts, specially designed to minimize the air carried along by the solvent.

- A demister by impaction has been implemented, as it provides the best compromise between a high efficiency and a low pressure drop. A low pressure drop is essential to keep the process pressure of the main evaporator as low as possible.

- Rectification tower: the rectification tower is fitted with a packing supplied by the Sulzer company, which provides a good efficiency, as well as low pressure drop.

- The mixer-settler bank devoted to washing the concentrated TBP recovered at the bottom of the distillation tower, is designed to process solvent with a high TBP content.

INDUSTRIAL RESULTS

The COGEMA UP3 TEO (for "Traitement des Effluents Organiques" = Organic Wastes Treatment) has now been in operation for more than a year. Even though this time is still short for drawing all conclusions, the first results are very encouraging. More than 500 m³ were processed before the end of 1990. The recovered diluent and solvent are recycled in the plant without any problem. The specifications of the products are easily met, and some results are significantly better than the specifications. Among them are the radioactivity of the recovered fractions and the residue rate which has been reduced significantly. This residue rate is currently well below 5%. The TBP grade of the recovered solvent is also significantly higher than the designed 60%. Both these results help to keep the volume of organic waste for disposal at a rate lower than the predicted value, which is very satisfactory.

CONCLUSIONS

For the new COGEMA plant UP2 - 800, an other TEO is currently under completion. It includes some process improvements, bearing mainly on the throughput and flexibility of the equipment.

This process has been selected for the JNFS future reprocessing plant at Rokkasho (Japan), after complementary studies performed by CEA and SGN for the adaptation of the distillation process to specific JNFS requests.

We are therefore now confident that such distillation units will soon become a standard item in any reprocessing plant.

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