

PEBBLE BED PYROLYSIS FOR THE PROCESSING OF ALPHA CONTAMINATED ORGANIC EFFLUENTS

Paul Luycx, and Jan Deckers

Waste Processing Departement, Belgoprocess, Dessel, Belgium.

ABSTRACT

In order to convert 17 m³ of spent solvents (20 vol. % of TBP in 80 vol. % Shellsol T) originating from former reprocessing on its industrial site, into a qualified product for underground disposal, Belgoprocess has chosen the pebble bed pyrolysis process. The basic process is patented by the German Nukem company. In order to adapt it to the needs of the specific waste batch to be treated, the assistance of several subcontractors was sought. According to the adopted flowsheet, the TBP is decomposed at a temperature of 500 °C, in underpressure and under a nitrogen atmosphere, into phosphoric acid, various butylene fractions and water, while the hydrocarbons volatilize in the reactor. The phosphoric acid is neutralized by magnesium hydroxide and the resulting pyrophosphate, together with the ashes, is collected in 200 l drums. The hydrocarbon vapours are sent through a candle filter to an afterburner chamber, where they are heated to 1150 °C under an excess of air, for their conversion to CO₂ and water. The off-gases are quenched, scrubbed and filtered before being released to the atmosphere. The solid end product of the process is embedded into cement. Approximately 1 drum of 200 l is produced per cubic metre of effluent treated.

Belgoprocess was constituted in 1984 as a subsidiary of Synatom, the Belgian company which ensures the supply of fissile materials for the Belgian nuclear power stations, to operate the various waste processing facilities on the site of Eurochemic's shut-down reprocessing plant. At the end of 1986, when recommissioning of the reprocessing plant was abandoned, Belgoprocess became the subsidiary of the Belgian national agency for the management of radioactive waste (called NIRAS in Dutch and ONDRAF in French), and was gradually integrated in the overall radioactive waste management policy of the country. In 1989, this integration was completed with the take-over of the activities of the waste department of the neighbouring nuclear energy research centre (SCK CEN). Since then, Belgoprocess has gained experience in the processing of a large variety of radioactive wastes, mainly originating from the nuclear fuel cycle.

THE PROBLEM TO BE SOLVED

Some 17 m³ of spent solvent, 20 vol. % of TBP in 80 vol. % of Shellsol T, used for the solvent extraction of uranium and plutonium from dissolved spent fuel during reprocessing by Eurochemic, in the early 1970s, should be converted into a qualified product, suitable for interim storage and underground disposal. Within the frame of a financing agreement between the Belgian state and the Belgian electricity producers, on the clean up of liabilities from the past, this waste is to be processed by the year 2000.

Erroneously, this solvent has been mixed in the past with other effluents. As a result, the batch comprises different phases: solvent, oil and aqueous solution. Each of these phases is polluted by the others. Suspended matter is present in all liquid phases, and a sediment layer is present at the bottom of the two storage vessels.

In a first remediation action, carried out in 1993, the 58 m³ of the three phase mixture was divided over two stainless steel storage tanks: 17 m³ of spent solvents and 31 m³ of aqueous waste in the one, and 4 m³ of oil and 6 m³ of aqueous waste in the other. Recent analyses of samples taken at various depths in the storage tanks indicated a specific alpha contents of up to 9 E4 Bq/l and a specific beta contents of up to 3.0 E5 Bq/l in the aqueous phase. The oil contained 1.9 E3 Bq/l alpha and 2.3 E3 Bq/l beta emitters. Both phases are sent to the incinerator onsite for further processing.

The solvent mixture has a specific alpha activity of up to 5.9 E5 Bq/l and a specific beta activity of < 1.5 E4 Bq/l. The sediment layer in the larger storage tank contains 4.8 E7 Bq/l alpha and 8.6 E6 Bq/l beta emitters; the sediment layer in the smaller storage tank contains 1.8 E6 Bq/l alpha and 1.5 E5 Bq/l beta activity. The main radioisotopes present are americium-241, caesium-137, cobalt-60 and antimony-125.

Spent solvents from reprocessing are degraded by radiation and chemical reactions.

Degradation products of the TBP are dibutyl phosphate, monobutyl phosphate, long chain dialkyl butylphosphates- and phosphoric acids. Degradation products of the diluent are nitroparaffins, aldehydes, ketones, carboxylic acids and organic nitrates. This degradation affects fission product retention, plutonium and uranium losses in the extraction cycles of the reprocessing plant, precipitates and build up of crud at the interphase. The solvent is periodically cleaned, and must eventually be replaced.

The batch of spent solvents had been transferred from Eurochemic to the former waste department of the SCK CEN for treatment in the pilot high-temperature slagging incinerator, in conjunction with solid alpha-contaminated waste. However, the development programme of this incinerator was stopped before the spent solvents could serve as a test batch.

EARLIER SOLUTION: EUROWATT

Research and development work at Eurochemic concentrated on the recovery of the solvent in the purest possible form, and decomposition of the TBP fraction by pyrolysis. Other possible treatments, such as incineration and incorporation of the TBP fraction into organic materials, were rejected because they suffered from several disadvantages: severe corrosion problems for incineration; important end volumes of waste for incorporation into organic materials, and inadequate quality of end products.

Eventually, the Eurowatt process was developed and demonstrated in a pilot unit in the early 1980s. The process consisted of: (1) the quantitative extraction of the TBP fraction carrying the degradation products and radionuclides by anhydrous phosphoric acid, using mixer-settlers, and the recovery of the decontaminated diluent phase; (2) the decomposition of TBP by pyrolysis in a wiped film evaporator at 220-240 °C, catalysed by phosphoric acid; into inactive volatile hydrocarbons and inorganic phosphoric acids; (3) disposal of the inactive organic compounds and conditioning of the phosphoric acids neutralised with calcium hydroxide, in conjunction with other medium-level effluents into bitumen.

Eurochemic treated 20 m³ of its oldest spent solvents, having a specific total activity of 5 E4 - 6.1 E5 Bq/l, the main radionuclides being ruthenium-106, antimony-125, caesium-137 and americium-241: of the order of 8.3 E4-1.0 E5 Bq/l. The operating results were very satisfactory, and aroused the interest of Cogéma. A test on a few cubic metres of spent solvents from La Hague indicated that the recovered diluent would meet specifications for reuse.

However, negotiations on the treatment of 100 m³ of solvents from La Hague were broken off, reportedly because of a problem of conflicting transport regulations for volatile organic liquids on the one hand and radioactive liquids on the other hand.

The use of the shut-down Eurowatt pilot facility for the present batch to be processed was taken into consideration in 1991, but not adopted. The Eurowatt process would only solve part of the problem, viz. the separation of the butylphosphate compounds, while the cost of updating and recommissioning the unit was estimated at 90 million BEF. Belgoprocess wanted a process in which all the component parts of the waste batch could be processed.

OVERVIEW OF STATE OF THE ART

A preliminary study on the state of the art, carried out in 1995, showed that practical experience on the processing of radioactive organic liquids was really scarce. At the nuclear energy research centre of Karlsruhe (KfK), spent solvents of their pilot reprocessing plant had been separated into a kerosene fraction and a TBP fraction. The slightly contaminated kerosene had been incinerated and the TBP was absorbed on polystyrol. However, the separation facility has been dismantled. At La Hague, a flash distillation process is used for the recovery of the diluent fraction in view of its reuse in the reprocessing plants.

Fluidized Bed Combustion of butylphosphates Compounds

At the end of the 1980s, a lab test on fluidized bed combustion was carried out at the waste department of the SCK.CEN. It was found that the solvent mixture of TBP/Shellsol T could be incinerated in a previously calcined limestone bed. The combustion performance at 750 °C amounted to 99 %. Only 1 % of the phosphorous in the feed was emitted through the off gases; 80 % remained in the bed and the rest was apparently eluated from the bed in the form of fine, partially phosphated lime particles. The behaviour of fission products was not investigated in this limited experiment. It was concluded that further development work was needed for the processing of radioactive materials.

Electrochemical processes

Various electrochemical processes for the decomposition of the solvent mixture into phosphoric acid, CO₂ and water have been developed, but no practical experience was built up. These processes were developed to treat organic effluents, resins, plutonium-contaminated solvents, etc.

According to the *Silver II process* of AEA Technology, Dounreay, UK, the organic material is oxidised by Ag²⁺ at a platinum lined titanium anode to CO₂ and water. The remaining phosphoric acid can then be conditioned into either bitumen or cement. Whereas the principle of the process is relatively simple, the application requires a complex and voluminous installation. An installation at Belgoprocess was estimated to cost 5 million £, while treatment of the Belgian waste batch at Dounreay was estimated at 2-4 million £, exclusive of transport costs.

According to the *wet oxidation process* of JGC, Japan, the organic compounds are oxidised at atmospheric pressure, using hydrogen peroxide as an oxidising agent and iron or copper as a catalyst. Tests were only carried out on inactive liquids and resins. This technique would have needed quite a lot of further development.

According to the *DETOX process* studied at Los Alamos National Lab., USA the organic material is decomposed by wet oxidation at 200 °C, under pressure, and with Fe³⁺ as a catalyst.

Feasibility for the spent solvent mixture is not applicable due to budget and licenses problems.

According to the *packed bed pyrolysis/silent discharge plasma process* of Los Alamos National Lab., USA, a packed bed pyrolyser with Al₂O₃ granules is used for the evaporation of the organic material into free radicals which are subsequently oxidised at ambient temperature in a plasma cell.

This process looked promising, as the organic waste is destroyed at relatively low temperature, in the absence of high pressures. Further investigation indicated that this process would be suitable for the spent solvents at Belgoprocess. However, the system had only been in operation with non radioactive materials. A proposed cooperation for the further development of the process for the treatment of active organic liquids could not be realised, because LANL did not obtain the required authorization from the American Department of Energy.

Pyrolysis

In 1984, the German Nukem company obtained a European patent for its process for the decomposition of spent solvents by pyrolysis in a stirred pebble bed reactor, using magnesium hydroxide as a neutralising agent for the butylphosphates compounds. The resulting hydrocarbons can be treated by post-combustion; off-gases are scrubbed and filtered before emission to the atmosphere, while the phosphoric acid is converted to the pyrophosphate and can be conditioned into cement. Nukem had treated some active TBP/Shellsol T mixtures on a semi-industrial scale, upon which the facility had been dismantled. Patent rights were sold to French, Swedish and Japanese companies.

In Sweden, this process was tested with inactive solvents and resins. No active solvents were processed. In Japan, a test facility was constructed, but no results have been published. In France, SGN have carried out extensive development work in a pilot facility near La Hague. In January of 1998, their MDS (French acronym for: mineralisation of solvents) facility was started up to treat distillation residues (more than 60 % TBP up to almost pure TBP) from the spent solvents of their UP3 plant.

THE ADOPTED PROCESS

After having obtained expert advice in Belgium and abroad, it was decided to adopt the Nukem process for the design and construction of an installation by Belgoprocess, and to rely on engineering services and technical assistance of SGN and the Belgian ENI (Electrical systems engineering). All process parameters, the feed pre-treatment, post-combustion and off-gas treatment systems were all developed by Belgoprocess.

Pyrolysis has the advantage over other processes in that the formation of semi-volatile fission products is minimalised in the reducing circumstances, and the isotopes remain with the solid pyrophosphate end product. The **process** developed comprises four steps:

- (1) the batchwise feed pre-treatment in which the liquid waste is mixed in well-defined amounts and in a well-defined sequence, with a neutralising agent and an emulsifier to obtain a homogeneous, stable mixture with the desired low viscosity;
- (2) the continuous decomposition of the feed at high temperature, in a stirred pebble bed by pyrolysis; volatile and vapourized hydrocarbons are swept by a nitrogen sparge through a candle filter; the neutralised phosphoric acid is converted into the pyrophosphate form and removed at the bottom of the reactor;
- (3) the separated butylene groups, and the vapourized fraction of kerosene and hydraulic oils are sent to an afterburner chamber operating at 1150 °C, and are converted into CO₂ and water with an excess of air;

(4) off-gases are quenched, purified by scrubbing and fine filtration and sent to the stack through absolute filters.

The **pebble bed pyrolyser** is originally of SGN design. However, Belgoprocess has considerably adapted and improved the reactor. It is a cylindrical reactor made of Inconel, containing steel balls, which are continuously circulated by a screw. The reactor is electrically heated, kept in underpressure and under nitrogen atmosphere. As the organic components volatilize in the reactor and the tributyl phosphate is decomposed, the phosphorus is bound to the neutralising agent in the form of pyrophosphate that deposits on the steel balls and is shaken off by the repeated collisions of the balls against each other.

The reactor has a grated bottom, leading to a cone which is equipped with a vibrator and a nitrogen sparge for fluidisation of the solid end products which are collected in a 200 l drum. Hydrocarbons and vapours from the pyrolysis reaction pass a candle filter unit which is regularly blown back into the cone.

Determination of the adequate **feed composition** and mode of preparation thereof, is of particular importance in the process. The feed to the pyrolyser consists of an aqueous solution of the neutralising agent and the mixture of TBP in Shellsol T. To obtain a homogeneous feed, an emulsion of the aqueous and the organic phase is made. The composition of the emulsion and the identification of the appropriate emulsifier are determined by a series of tests in the process control lab of Belgoprocess. The most relevant results of these lab scale tests so far can be summarized as follows:

- Emulsification is a process that is very sensitive to a number of parameters; tests should thus be made in conditions which are representative for active operational conditions.
- Emulsification of inactive solutions is absolutely not representative for emulsification of radioactive spent solvents. This means that emulsification tests for active operation have to be performed on real waste samples; for the cold tests a specific inactive mixture has to be prepared with comparable viscosity to that of active emulsion.
- Stable oil in water emulsions could be easily made when starting out from simulated organic solutions, but not when using real solutions.
- It was only possible to make a low viscosity water in oil emulsion with the active solvent mixture. It partially separates in phases when stirring is stopped, but the emulsion is restored when stirring is reactivated.
- Emulsification is also sensitive to the sequence of adding the different components.
- During cold testing of the facility, it proved that the lab scale tests are representative for the emulsification process at industrial scale.
- The nature of the emulsifier, the composition of the emulsion and the sequence of adding the components must be determined by lab scale tests on a representative sample for each type of organic solution to be pyrolysed.
- The amount of water should be limited in the emulsion, in order to avoid large amounts of steam in the flue gases, which would require larger filters at the outlet of the reactor.
- The viscosity of the emulsions must be limited such that it is compatible with a good mixing in the feed pre-treatment vessel.

As it was the intention, from the start, to maximize use of existing equipment and plant, the pyrolysis unit is installed in an existing alpha-tight area, in which all utilities are present. However, it proved that the capacity of the existing off-gas treatment is much too big for the pyrolyser system. In order to allow a precise control of the underpressure in the reactor, the construction of an adapted off-gas system was required.

OPERATING PROCEDURE

The hydraulic oil in the smaller storage tank and aqueous phases in both storage tanks are removed as efficiently as possible and sent to the low-level waste incinerator onsite, before the pyrolysis campaign is started.

Transfer. The remaining solvent mixture is transferred per batch of 1 m³ to the feed preparation tank of the pyrolysis facility. A mobile pump unit is used for transferring the solvent mixture through an existing double-walled high-density polyethylene duct to the transfer tank of the alpha-tight area in which the pyrolysis unit is installed.

Feed pre-treatment. After sampling for analysis, the feed pre-treatment consists of the addition, in well defined proportions, and in a well defined sequence, of a neutralising agent, water and an emulsifier to obtain a homogeneous and stable feed composition with low viscosity.

Reactor feeding. The feed composition is circulated at constant pressure, and part of it is injected into the stirred pebble bed reactor. Circulating the feed composition has the additional advantage of maintaining the emulsion stable. The reactor is fed through one of the two installed injection lances, which are cooled, so that the pyrolysis reaction only takes place on the pebble bed. A small nitrogen volume is added to the feed, in order to avoid blockage of the lances. The feed rate is 12 kg/h.

Pyrolysis process. In the pyrolyser, the TBP is decomposed into butylene fractions and phosphoric acid. The kerosene and water evaporate. The phosphoric acid is bound by the neutralising agent and converted into the pyrophosphate form. The latter, together with the excess of neutralising agent are removed through the grate at the bottom of the reactor. The hydrocarbons, water vapours and nitrogen are sent through candle filters, equipped with a blow-off system, to the afterburner chamber. All pyrophosphate is thus separated by the filters and removed from the reactor through the cone as a solid end product.

Post-combustion. The hydrocarbons are post-combusted with an excess of air, at a temperature of 1150 °C. Their residence time in the afterburner chamber is 3 seconds at the most.

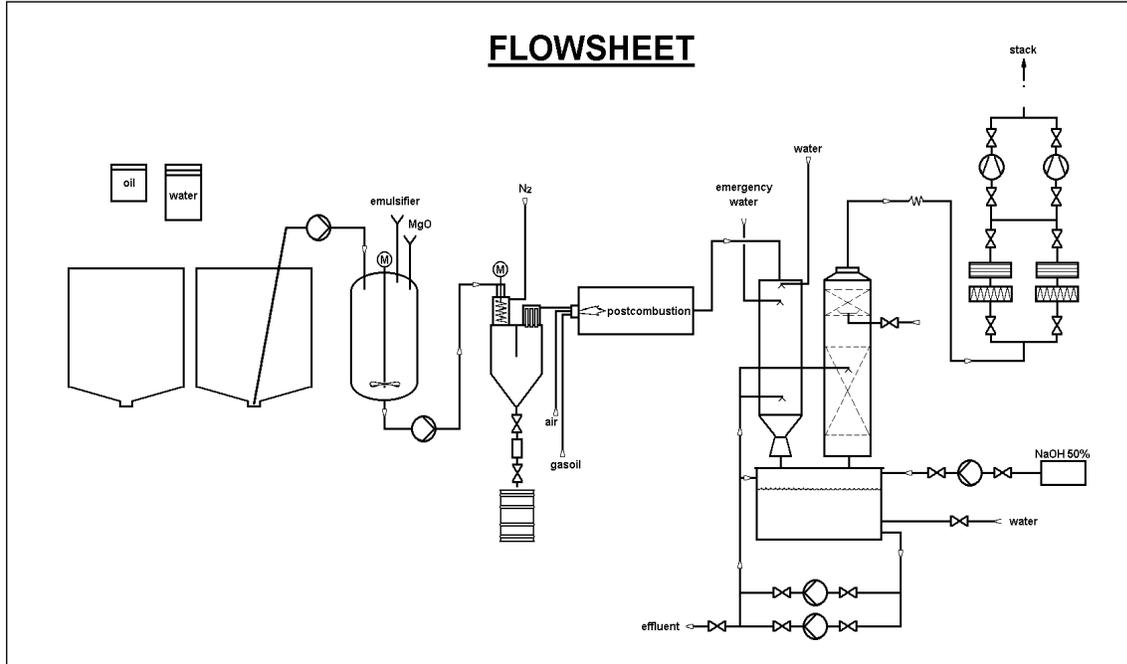
Off-gas purification. Combustion gases are quenched to cool to about 80 °C. An emergency cooling is provided in order to remove the gases safely in case of accident. In a first step, particles up to size 3 µm are trapped in an ejector-venturi and HCl and SO₂ are neutralised a first time. In a second stage, HCl and SO₂ are further neutralised in a packed bed absorption column. The presence of sulphur and chlorine will be minimal, as they only originate from the emulsifier and the oil used for the post-combustion.

The purified off-gases are sent through a pre-filter and absolute filter, before being released through the stack. A redundant filtering system is installed in parallel and can be used as a back-up at any moment.

Safety features. The flash point of the solvent mixture, measured according to ISO 3680-1983, is 58 °C, i.e. three degrees above the limit requiring zoning. Normally, zoning would be applied around the pyrolysis reactor, but as operations proceed at underpressure and in a nitrogen atmosphere, zoning could be minimized. Both underpressure and presence of oxygen is constantly monitored in the reactor area. When preset limits are exceeded, automatic interlocks prevent the pyrolyser from operating. Likewise, in the post-combustion and off-gas treatment area, interlocks and alarms, flame and temperature monitoring, control of underpressure, circulation of cooling water, liquid level in scrubber, etc. ensure that operation can only proceed when preset conditions are met.

Explosion and oxygen measurements above the solvent mixture in the storage tank did not indicate any dangerous situation.

Operations are remotely controlled. Once a week, workers have to enter the area to exchange the drum filled with pyrophosphate and dust for an empty one, and to prepare a new feed batch. The treatment of the spent solvents and the rinsing solutions of the storage tanks (in all some 20 m³) will take 6 months of operation in a three shift schedule, 5 days per week. Per m³ treated, one 200 l drum will be filled with solid end product. These drums will be closed and embedded in cement into 400 l drums.



HAZOP STUDY

Working principle, design, equipment, process flows, monitoring, control ... all parameters were checked step by step in a HAZOP study, from the transfer of the waste batch to the pyrolysis unit to the removal of the end product on the one hand, and the release of purified off-gases on the other hand. This resulted in a further fine tuning of the plant, and an optimisation of the operating procedures.

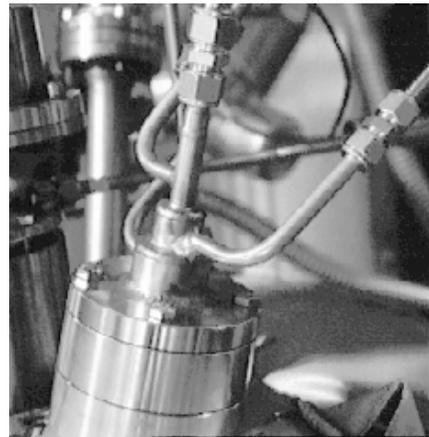
COLD TESTS

The system has been set up in a non-controlled area to be cold tested. The different sub-systems are mounted on skids and can be easily dismantled and set up again. Cold tests are performed on actual scale, because it is all but impossible to realise a stable metering of the feed of less than 10 kg/h. Performing tests in a cold area allows easier access, avoids the production of "suspect" wastes, and costs less. During the cold tests, which took three months in the second half of 1998, the operators were trained and could get familiar with the installation.

A simulate of the active emulsion was prepared to check the composition parameters, pebble bed load, operating temperatures, combustion performance and off-gas treatment. It showed that the pyrolysis reaction performed excellently. No phosphorus, nor any neutralising agent was found in the off-gas purification system. No undue wear could be detected upon inspection of the various mechanical systems.



Pebble bed pyrolysis unit, as installed for cold testing at Belgoprocess



Injection lance

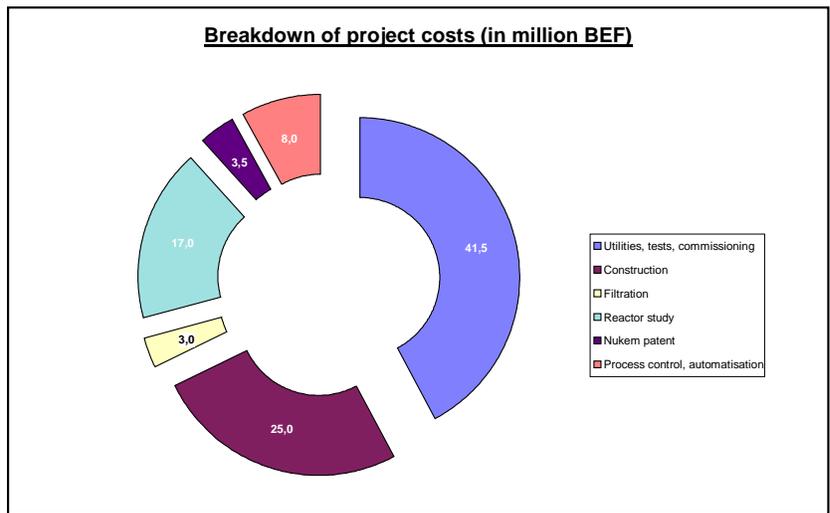
ADDITIONAL FEASIBILITY TESTS

It was decided to perform additional feasibility tests for the treatment of contaminated resins, and of combustible alpha-contaminated solid waste. Resins are fed as such to the pyrolyser; solid combustible waste is shredded to very small pieces. Both possibilities would definitely add to the utilization of the facility, as the incinerator onsite can only process low-level resins with very low alpha contamination, while combustible alpha-contaminated waste has not yet been provided for in the waste processing schemes of Belgoprocess.

These feasibility tests will take until the second half of December, 1998. Afterwards, the installation will be moved to the alpha-tight area. Active operation has been rescheduled to the second half of 1999, as the operators will first have to complete another job onsite.

COSTS

Study, design, construction and commissioning of the pyrolysis facility cost 98 million BEF, 40 % of which is earmarked for cold and hot testing, commissioning and analytical investigations. The actual treatment of the 17 m³ of spent solvents and estimated 4 m³ of rinsing solutions to remove the sediment from the storage tanks, will cost another 40 million BEF.



PRELIMINARY CONCLUSION

Belgoprocess is presently ready to become the second nuclear operator to apply the pebble bed pyrolysis for the processing of real radioactive spent solvents.

Since the restructuring of the back-end of the nuclear fuel cycle was completed in Belgium, important investments have been made in bringing existing plant up to date, replacing obsolete waste processing facilities, and adding new facilities, allowing the application of the best available techniques. Waste processing experience at Belgoprocess covers the whole range of solid and liquid radioactive wastes.

The company has developed an integrated waste management policy aimed at minimal occupational exposure, minimal discharges to the environment and a maximum reduction of waste volumes for ultimate disposal. Belgoprocess is ready to share its comprehensive knowledge and experience with clients all over the world.