Thorough Chemical Decontamination With the MEDOC Process: Batch Treatment of Dismantled Pieces or Loop Treatment of Large Components Such as the BR3 Steam Generator and Pressurizer

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ABSTRACT

The dismantling of the BR3-PWR reactor leads to the production of large masses of contaminated metallic pieces, including structural materials, primary pipings, tanks and heat exchangers. One of our main objectives is to demonstrate that we can minimise the volume of radioactive waste in an economical way, by the use of alternative waste routes, such as the clearance of materials after thorough decontamination.

The SCK•CEN uses its own developed chemical decontamination process, so-called MEDOC® (MEtal Decontamination by Oxidation with Cerium), based on the use of cerium IV as strong oxidant in sulphuric acid with continuous regeneration using ozone. An industrial installation has been designed and constructed in close collaboration with Framatome-ANP (France). This installation started operation in September 1999 for the treatment of the metallic pieces arising from the dismantling of the BR3 reactor. Since then, more than 25 tons of contaminated material including primary pipes have been treated batchwise with success. 75 % of material could be directly cleared after treatment (Activity lower than 0.1 Bq/g for ^{60}Co) and the other 25% free released after melting (activity lower than 1 Bq/g).

The SCK•CEN performed in April 2002 the closed loop decontamination of the BR3 Steam Generator by connection of the MEDOC plant after few adaptations. The decontamination was done within 30 cycles in 3 weeks with consecutive steps like decontamination steps (injection of the solution into the SG) and regeneration steps with ozone. In total, 60 hours of decontamination at 70°C and 130 hours of regeneration were needed to reach the objectives. The tube bundle (600 m^2) was attacked and about 10 µm representing more than 41 kg of stainless steel and 2.06 GBq of ^{60}Co was dissolved into the solution. The residual contamination measurements made directly into the water box are still going on, however it seems that the objective to reach the free release criteria after melting is achieved. The next decontamination operations of large components concern the primary pumps (*2) and the pressurizer and are foreseen in October 2002. The decontamination studies of large components take into account the technical aspects, the radiological and classical safety aspects, as well as the financial aspect.

OVERVIEW OF THE BR3 DISMANTLING ACTIVITIES

The BR3 (for Belgian Reactor 3) was the first PWR installed in Europe. In service since 1962, it was shut down in 1987 after 25 years of operation. It is a small reactor with an electric power of 10 MW_{el}, originally used for the training of operators of future power plants and then mainly used for testing of prototype advanced fuel design (MOX, Gadolinium fuels, high burnup...). At the end of its operating life, it was selected as one of the four pilot decommissioning projects by the European Commission in 1989, in the framework of its five-year plan of Research and Technological Development on decommissioning of nuclear installations.

The main steps of the decommissioning programme up to now were

- the full system decontamination of the primary circuit in 1991,
- the dismantling of highly active internals: 2 sets in 1991-1995,

- the dismantling of the auxiliary circuits, started in 1995 and is still ongoing,
- the construction of thorough decontamination plants of metallic pieces,
    - wet abrasive process in 1996,
    - thorough Chemical MEDOC Process in 1999,
- the dismantling of the reactor pressure vessel in 1998 – 2000 [1].

The dismantling produces a variety of metallic wastes, some of them are suitable for the MEDOC treatment:

- Stainless steel equipment with crud deposit (1000 to 20,000 $Bq.cm^{-2}$): reservoirs, heat exchangers, primary piping, auxiliary circuits,
- carbon steel equipment slightly (10 to 200 $Bq.cm^{-2}$) or heavily contaminated (more than 1000 $Bq.cm^{-2}$): reservoirs, heat exchangers and piping,
- carbon steel equipment with stainless steel cladding or with stainless steel parts: typically the pressurizer, the steam generator, heat exchangers.

To treat the various types of contaminated materials, it is necessary to have a variety of decontamination processes, such as physical methods (wet or dry abrasives) and chemical methods (aggressive processes with regeneration of reagents).

PRINCIPLE OF THE MEDOC PROCESS

The MEDOC® [2] process that was selected is based on the use of cerium IV as strong oxidant in sulphuric acid with continuous regeneration using ozone. According to the thermodynamic data, the ceric ion should not exist in aqueous solution since its standard potential (E_0 = 1.44 V) is higher than the one related to the oxidation of water. However, the kinetic of the oxidation of water by the ceric ion is slow enough to stabilise the latter.

Cerium IV dissolves both the oxide layer and the base metal as show in the following equation:

$$nCe^{4+} + M \longrightarrow nCe^{3+} + M^{n+}$$, where *n* is the valence of the considerated metal

The removal of about 10 µm is generally sufficient to completely remove the contaminated layer and to reach the free release level even with highly contaminated samples (e.g. samples covered with PWR crud or samples of hot cells strongly contaminated in ^{137}Cs and alpha).

The cerium IV in mixture with sulphuric acid was chosen as oxidant for the chemical decontamination over other traditionally employed oxidants for several reasons:

- The cerium IV can be regenerated and recycled in the process.
- The decontamination can be achieved in one step compared to several steps processes where an oxidation / reduction step and several cycles are needed.
- The cerium IV dissolves both the oxide layer and the base metal with a high corrosion rate and leads to very low residual contamination on treated pieces.
- The neutralisation of cerium VI and the treatment of the solution for final conditioning are simple.

During the decontamination step, the cerium IV is consumed to give cerium III and the solution looses its oxidising power (Figure 1). To maintain a high corrosion rate for a treatment time as low as possible, the consumed cerium IV is continuously regenerated with ozone [4].

The ozone process shows some advantages:

- the ozone production is done outside the controlled area so that maintenance can be done in "non radioactive conditions";
- in normal operation, there is no H_2 production with its associated risks;
- ozone is a toxic gas but it can be detected very easily due to its strong smell (threshold value: 0.05 ppm);
- the gas-liquid contactor is a simple equipment with easy maintenance.

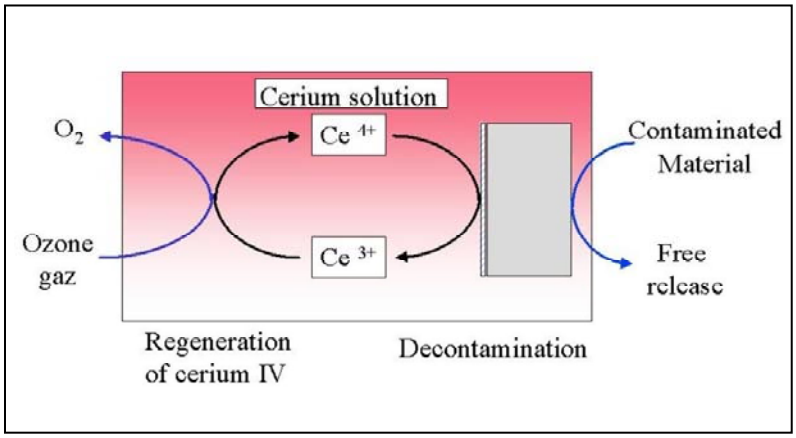


Figure 1: In the MEDOC process, the decontamination step and the regeneration step occur in the same solution at the same working temperature

The ozone oxidises the cerium III into cerium IV in the acidic decontamination solution:

$$O_3 + 2Ce^{3+} + 2H^+ \longrightarrow 2Ce^{4+} + O_2 + H_2O$$

The regeneration is performed using a static mixer with mixing elements in PVDF: co-current contactor with gas and liquid flow upwards. Static mixers are particularly interesting for their compactness. An efficiency between 65 and 75% could be reached at the 80°C operation temperature for an ozone concentration of 100 $g.m^{-3}$. For its compactness and much lower investment cost, a static mixer developed by Sulzer was selected and the design adapted for the industrial application.

DESIGN OF THE INDUSTRIAL SCALE CHEMICAL DECONTAMINATION UNIT

An industrial installation has been designed and constructed in close collaboration with Framatome-France with Belgian and French constructors. This installation started operation in September 1999 for the treatment of the metallic pieces arising from the dismantling of the BR3 reactor. The main objective is to treat the pieces to reach the free release levels [3].

A simplified flow sheet (Figure 2) of the installation explains the process:

- A basket containing between 500 to 1000 kg of metallic pieces is loaded inside the decontamination reactor.
- The decontamination loop comprises a decontamination reactor, a buffer tank, a circulating loop and a static mixer where the ozone is injected. Ultrasonic transducers surround the basket to promote the decontamination process. The decontamination is performed at 80°C in a sulfuric acid solution loaded with ceric sulfate. The consumption of the ceric ions by reaction with the metals is compensated by the continuous regeneration process with ozone laden oxygen. The decontamination of a batch takes maximum one day.
- After decontamination, the basket is removed from the decontamination reactor and transported inside the rinsing reactor. The rinsing is performed in a filtered closed loop with ultrasonic transducers surrounding the basket to promote the rinsing effect.

- When the rinsing is finished, the basket is placed on a drip tray to allow drying of the pieces. The pieces are then manually transferred inside a clean container to go to the measuring station where each piece is individually controlled for contamination.
- The decontamination solution which can contain some insoluble particles or undissolved oxides can be batchwise filtered.

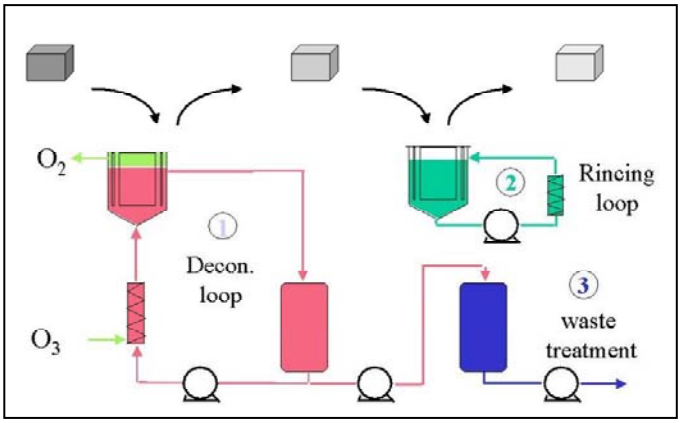


Figure 2: Simplified flow sheet of the installation

Safety precautions

Due to the combined radioactive and chemical hazards associated to this operation, a lot of safety precautions are taken into account [4].

- the construction materials have been selected to resist to the aggressive process conditions,
- the unreacted ozone is thermally destroyed before its release in the ventilation system,
- ozone and hydrogen detectors are installed at various points in the process lines and in the installation rooms,
- the rooms are ventilated with two independent filtration/ventilation systems.

The control philosophy and the man-machine interface have been designed to bring automatically the installation to a safe-stop condition in any case. For example:

- a detection of hydrogen above a certain level (below the 4% Low Explosion Limit) in the process line or in the rooms, due for example to the presence of carbon steel in the materials to decontaminate, leads to an automatic stop of the process (automatic transfer of the solution in the buffer tank, extra dilution with air)
- a detection of ozone in the rooms leads to an automatic stop of the ozoner;
- liquid leakages collected in drip tanks are detected and manual or automatic stop is actuated.

Furthermore, all process parameters and exploitation including dose rate, ozone and hydrogen concentration, level in tanks, redox potential and so on are monitored and saved into the computer. The systematic exploitation of these results improve our experience and give significant information about the decontamination process allowing its optimisation.

BATCH TREATMENT DECONTAMINATION

Up to now, contaminated materials have been successfully decontaminated using a batchwise technique in MEDOC plant. Contaminated materials are attacked with an average corrosion rate of about 2.5 µm.h^{-1}.
Since then, more than 25 tons of contaminated material, including primary pipes (Picture 1), have been treated batchwise with success. 75% of material could be directly cleared [5] after treatment (Activity lower than 0.1 Bq/g for ^{60}Co) and the other 25% free released after melting (Activity lower than 1 Bq/g).
The industrial scale MEDOC plant used at BR3 allows the batchwise treatment of 0.5 tonne/day of highly contaminated materials e.g. up to 20,000 Bq.cm^{-2} βγ and can achieve decontamination factors higher than 10^4.

Picture 1: few primary pipes decontaminated with MEDOC

DECONTAMINATION OF LARGE EQUIPMENTS USING THE MEDOC PLANT

Up to now, the decontamination was accomplished batchwise in the decontamination reactor loaded with contaminated material. The SCK•CEN uses now the MEDOC plant to decontaminate large components before cutting them. This operation concerns mainly the primary side of the BR3-steam generator (SG) and the pressurizer. The SCK•CEN performed in April 2002 the closed loop decontamination of the BR3 Steam Generator by connection of the MEDOC plant after few adaptations.

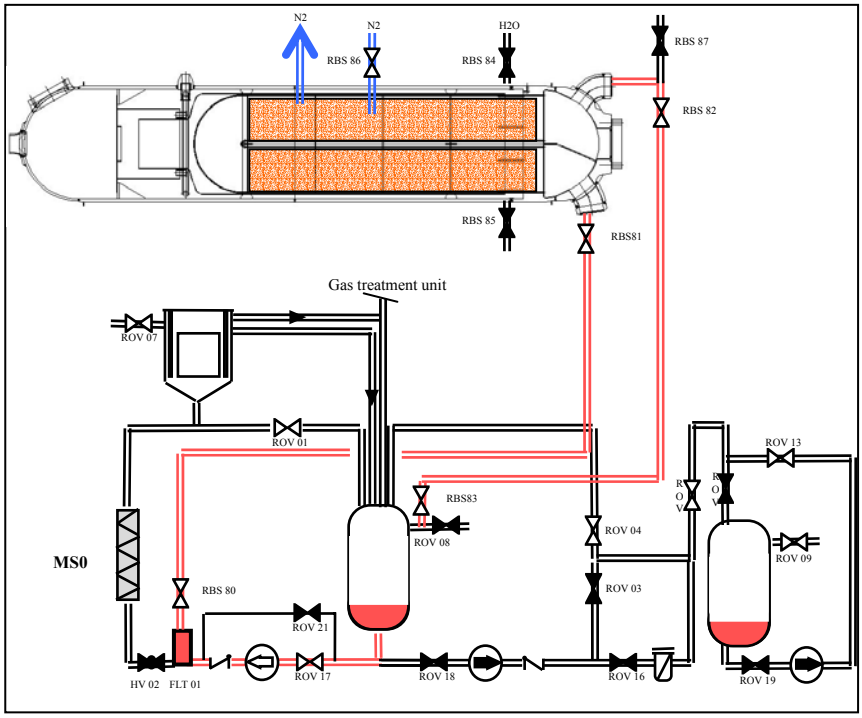


Figure 3: The BR3 Steam generator connected with MEDOC

The BR3-steam generator is a vertical drum, approximately 8 meters high, 1.5 meters in diameter for an associated weight of about 30 tons. The unit consists basically of a primary head, a tube sheet and a tube bundle enclosed with a shell. The tube bundle with 1400 tubes in type 304 stainless steel represents a total surface of the primary side of about 600 m^2. One specificity of the BR3-SG is that no tubes are plugged and no primary-to-secondary fluid leakages are mentioned in the historical exploitation data. The total access to the primary side surface allows us to make the overall decontamination in one piece.

The MEDOC plant has been modified to provide departure of the decontamination solution to the SG (Figure 3). Flexible PTFE lines over 42 meters and temporary valves have been used to connect the components to each other. Few components of MEDOC were adapted for the operation. This is the case of the main pump which has to allow sufficient pressure and a flow rate of about 50m^3/h.
Prior to the decontamination, the SG has been removed from its actual position and placed horizontally to allow the total filling up of the primary side with the decontamination solution.

The decontamination solution was circulated through the SG during the decontamination step at 70°C. The temperature was maintained constant with the small 40 kW heater of MEDOC without auxiliary power. Due to the large surface area of the primary side in contact with the solution, the cerium IV was consumed within 2 hours. In these conditions, the corrosion rate was close to 0.2µm/h. The low corrosion rate compared to the treatment in batch with MEDOC is probably due to the consumption of cerium against the time without regeneration and the low turbulences inside the tube bundle (without ultrasound and low flow rate in each tube). 30 decontaminations cycles of 2 hours were needed to remove 10 µm of base metal (41kg of material) inside the tube bundle and reach the target in term of residual activity.
Between each decontamination step, the steam generator was drained to allow the regeneration of cerium IV directly in the MEDOC plant. The regeneration was done during 4 hours corresponding to the regeneration of 3.4m^3 of the decontamination solution. The overall time for the decontamination was about 60 hours and 130 hours for the regeneration step.
After the first 15 cycles, the SG was rotated and the connections displaced to reverse the flow inside the tube bundle and allow a homogenous attack everywhere on the primary side. During the firsts new cycles (number 16 and 17) the corrosion rate was higher and closed to 0.4µm/h.

Workload

The total workload is about 1700 man-hours for the SG and the pressurizer decontamination. The preparation itself takes about 6 months and 50% of the work load; the operation itself only 4 weeks and 40% of the workload; the post operation takes 2 weeks and 10% of the workload.
The decontamination of the steam generator goes for 15 working days with two teams working in shift.

Safety precautions

The main risk of this operation, except eventual leakage through flexible junction tubing, was the presence of primary-to-secondary fluid leakage. The decontamination solution could be in contact with the secondary side of the SG made in carbon steel. To prevent explosive atmosphere associated with the hydrogen production, the secondary side will be placed under inert nitrogen atmosphere. In case of hydrogen detection, it was foreseen to spread water inside the secondary side to remove all acid leakage. No Hydrogen was detected during the operation; however, the measurement based on thermal conductivity of gas was difficult due to the presence of moisture inside the secondary side.

Radioactive waste production

After decontamination, the effluents were removed from the MEDOC plant to two small transport containers. The steam generator was rinsed 3 times with 3 m^3 of water in circulation between MEDOC and the component. Due to the presence of sludge inside the tube bundle, it was also manually rinsed (Picture 2) directly into the primary head with pressurised water.

Picture 2: the steam generator during final rinsing and inspection

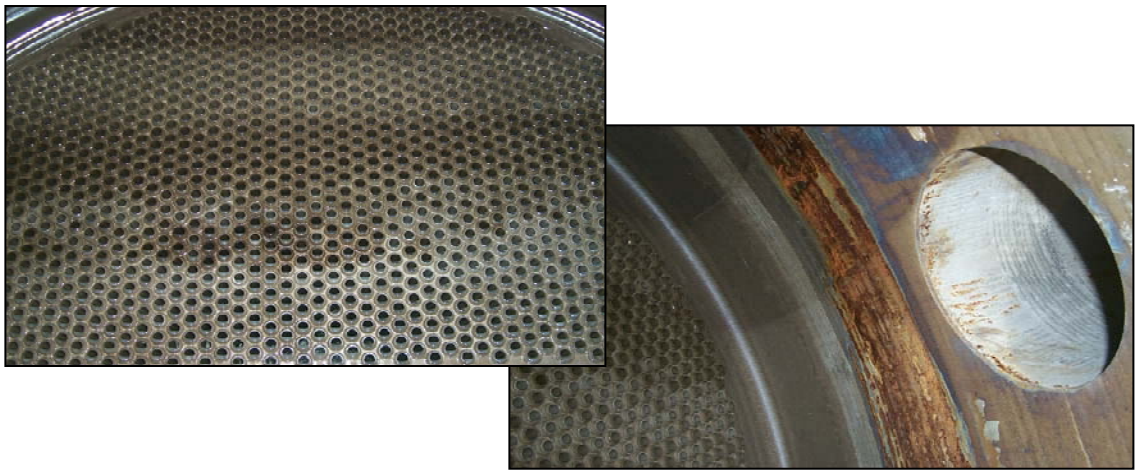
The secondary waste production was the 3.4m^3 of decontamination solution containing about 2.06GBq of ^{60}Co. This effluent follows the same route which has been set up in collaboration with Belgoprocess. The post operation effluents used for the rinsing was close to 10m^3 and are evacuated as traditional operational effluent.

Results

The purpose of this operation was to reach a sufficient decontamination factor to reduce the dose rate and free release the material after melting. For the SG, the initial contamination level of the primary side was about 335Bq/cm^2, the decontamination factor target is 500 - 1000 to have a residual contamination below 1 Bq/cm^2. It is difficult at this time before cutting to have values for the residual contamination. However, there is no more free contamination and the mean dose rate inside the primary head, cold legs and hot leg is lower than 3µm/h. Only few spot lightly contaminated (200µm/h) was detected:

- On the partition plate, it was due to the presence of screws which have been removed.
- On the welding between the primary head and the external secondary shell where the metal is rusted (see Picture 3).
- On the flange of the primary head (carbon steel), which was not in contact with the decontamination solution.

These two last parts will be decontaminated later using physical or mechanical techniques.



Picture 3: The tube bundle and a cold leg view inside the primary head

During all the operations, the radiation at the outside of the steam generator was monitored using a NaI spectrometer. The activities for ^{60}Co initially equal to 340 cps decreases to 8.7 cps which is lower that the background in this area.

DECONTAMINATION OF THE PRESSURIZER

The next decontamination operations of large components concern the primary pumps (*2) and the pressurizer and are foreseen in October 2002.
The pressurizer is a vertical drum, approximately 5 meters high, 1 meter in diameter for an associated weight of about 12 tons. The internal part which was in contact with primary coolant, is clad with type 304 stainless steel. The gross internal volume is 2.79m^3 of which 35 litres are occupied by the heater wells and their support. The total internal surface area is 20m^2. The decontamination process will be the same as used before for the steam generator excepted for the volume of decontamination which can be lowered. In order to reduce the volume of secondary waste, the pressurizer will not be filled up entirely like the SG but the solution will be injected through a spray nozzle mounted in the top of the pressurizer. The level of solution in the pressurizer will not exceed the top of the heater wells. Considering the contamination level of the internal part close to 7000Bq/cm^2, the decontamination factor target is 10,000 to have a residual contamination below 1Bq/cm^2. To reach this decontamination factor, it is foreseen to remove 30µm of contaminated metal over all surface of 20 m^2.

CONCLUSIONS

Up to now, contaminated materials have been successfully decontaminated using a batchwise technique in MEDOC plant. Contaminated materials are attacked with an average corrosion rate of about 2.5µm.h^{-1}.
Following decontamination using the MEDOC process 75% of treated materials have very low residual contamination (lower than 0.1Bq.g^{-1}) after treatment and this may be disposed of as free release decontaminated material. The remaining 25% has a residual activity lower than 1 Bq.g^{-1} and may be disposed of as free release route after melting. The industrial scale MEDOC plant used at BR3 allows the batchwise treatment of 0.5 tonne/day of highly contaminated materials e.g. up to 20,000 Bq.cm^{-2} βγ and can achieve decontamination factors higher than 10^4.
The BR3 team uses now the MEDOC plant to decontaminate large components in one piece before cutting them.
The decontamination of the steam generator was done in April 2002. The overall time for the decontamination was about 60 hours and 130 hours for the regeneration step.
The objective of this operation is to reach sufficient decontamination factor to free release cutting materials after melting. 30 decontaminations cycles of 2 hours were needed to remove 10µm of base metal (41kg of material) inside

the tube bundle and to reach the target in term of residual activity. There is no more free contamination inside the tube bundle and the mean dose rate inside the primary head, cold legs and hot leg is lower than 3µm/h.
The next decontamination operations of large components concern the primary pumps (*2) and the pressurizer and are foreseen in October 2002.

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