REACTOR COOLANT CIRCUIT DECONTAMINATION

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ABSTRACT

Experience in the chemical decontamination of the primary circuit of small reactors is reviewed and current developments discussed for both in-service and decommissioning purposes. Methods applied as part of planned maintenance and decommissioning for dose minimization are also described.

INTRODUCTION

Royce and Associates Ltd (RRA) have been involved in the decontamination of nuclear reactor plant for over 20 years as a part of a dose management strategy to minimize operational and maintenance man-doses on small PWR's. More recently decontamination prior to decommissioning has been considered for old reactor plant. Justification is more difficult with regard to decommissioning as man-dose savings only apply during the following dismantling and waste handling stages, which can nearly always be delayed. Deferment, as well as putting back the capital spend also allows the activity inventory to reduce by decay.

An integral part of planning both for decontamination and decommissioning is to estimate the man-dose which would ensue for various dose management options. For example, in some cases local shielding may be a more cost effective method than decontamination. Computer programs developed by RRA provide a technique to estimate the man-dose for various dose reduction methods. Together with cost benefit analysis the codes provide evidence that the chosen options comply with the ALARP principle.

All the initial development of decontamination processes and applications carried out to date have been on plants with spinal type oxide films. In the future mixed material plants will require decontamination and therefore new processes compatible with these materials are being evaluated. In addition as pressures with regard to waste disposal have increased, it has become important to optimize plant clean-up and to consider volume reduction methods where appropriate. A particular objective has been to integrate the waste management with the decontamination process. The various factors which need to be considered to ensure the ALARP principle is applied to the whole process is shown in Fig. 1.

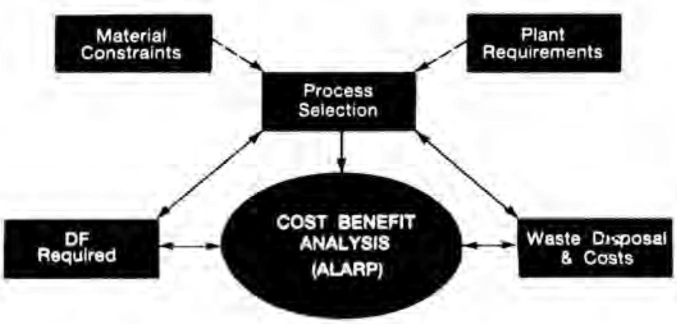


Fig. 1. Decontamination process development logic.

DOSE MINIMIZATION DURING DECONTAMINATION AND DECOMMISSIONING OF REACTOR PLANT

It is during the design/development stage of a decommissioning or decontamination project that the potential for the greatest dose savings arise. The opportunity exists to choose options that are least dose intensive, and also to have a major impact on the way the work is carried out.

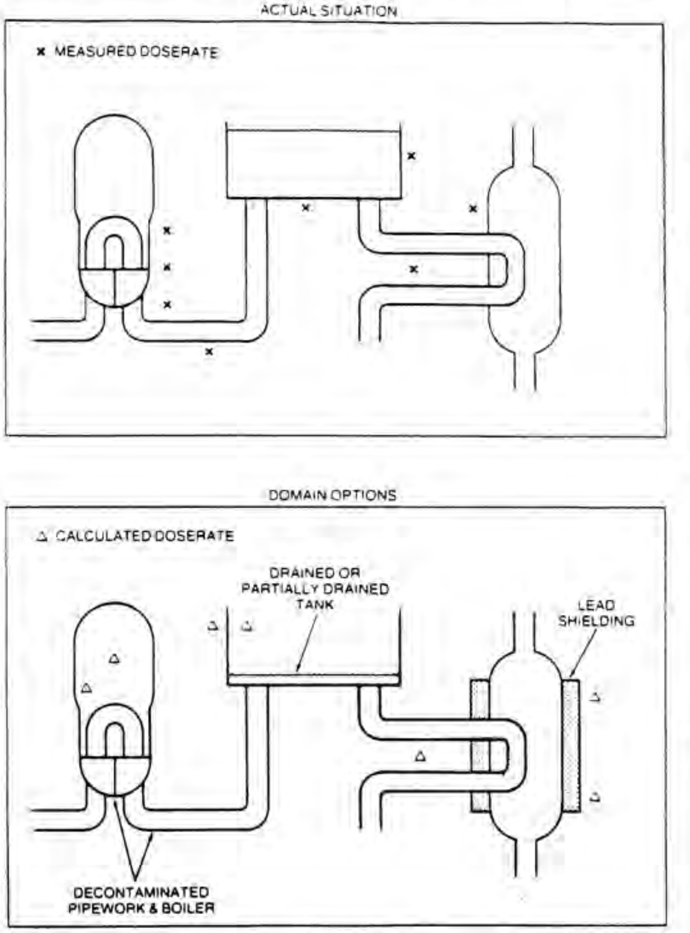
The following information is important for dose management planning:

1. Activity levels and their distribution. Knowledge of where the source resides can be used to determine in which order items should be removed. Knowledge of quantity of activity is needed to assess the type of waste that will be dealt with and its method of transport and ultimate disposal.
2. Dose rates both internal and external to components. This information is needed to decide which components will require shielding or whether decontamination is called for. It also helps to define the need for robotics if dose rates are high, and what kind of radiation environment personnel will be working in.
3. Doses for specific tasks or individuals. This can be used to determine the number of people required for each type of work, and to identify who is likely to be the "critical group" of workers. Quantities such as the overall dose, the maximum dose to an individual, the average dose etc. can be derived and compared to any dose targets that were set during the justification phase.

If there is no previous experience of planned work then a calculational technique is the only route available to obtain such information. A calculational technique has the added advantage of being able to assess the collective dose for several options, identifying the lowest dose option, and demonstrating the application of the ALARP principle. The code DYDAS/DOMAIN, developed by Rolls-Royce and Associates, provides such a calculational capability.

DYDAS/DOMAIN can calculate gamma sources, doserates and doses from a complex physical structure containing distributed activity sources. In addition the code can be used to investigate the effect on doserates, and hence doses, of various options eg. installing extra shielding, removing sources, draining or filling of components and decontamination of all or some of the components. A simple model is shown in Fig. 2.

If activation products are a major contributor to the source activity these can be calculated via other codes eg. CAIRN which has been developed by Rolls-Royce and Associates and whose prime application is to calculate isotopic



An Illustration of Dose Reduction Options Capable of Being Analysed by DOMAIN

Fig. 2. An illustration of dose reduction options capable of being analysed by DOMAIN.

activities within complex reactor components for decommissioning and disposal programs.

From one set of doserate measurements the DYDAS/DOMAIN route can be used to calculate the data required in planning the dose management of a decommissioning and/or decontamination program, and can determine the optimum method of working without the need for additional measurement.

DECONTAMINATION EXPERIENCE

In the early 1970's there was pressure on reducing the man-dose which was accrued during planned maintenance of the small nuclear plants. Decontamination prior to maintenance was seen as a potential method for reducing this dose. The plants are operated under typical PWR primary chemistry with hydrogen dosed coolant. Plant films are of a spinel type oxide with a chromium rich layer. Various processes were considered and evaluated. It was soon ascertained that a two stage process was essential. The first stage is required to leach out chromium from the oxide film, whilst the second stage performs the actual decontamination by dissolving the remaining film. The final process selected by RRA was a proprietary two-stage treatment comprising:

First Stage: Turco 4502 (inhibited alkaline permangate) used at ~25% concentration.

Second Stage: Turco 4521 (inhibited mixture of oxalic and citric acids with added ammonia to adjust pH) used at ~6% concentration.

An inhibitor was necessary to maintain acceptable corrosion rates on some alloys in the reactor circuit. The process was applied to the loop and steam generator of the primary circuit. Large pumps were required for injecting the stage chemicals. Interstage clean-up was achieved by several ram flushes with demineralized water. The resulting effluents were mixed to precipitate large volumes of manganese dioxide with coprecipitation/adsorption of radioactive species. The sludge was filtered and cemented into drums for disposal. A simplified system diagram of the decontamination waste treatment plant and its fit-up to primary circuit of the reactor is shown in Fig. 3. The process proved highly effective with typical decontamination factors (DF) of 10 achieved on the loops and steam generators. However, the process was perceived to have deficiencies with regard to the high fit-up dose, the large volumes of waste, the extent of waste treatment required and rapid recontamination of the primary circuit when back in-service. As a consequence a new process was sought that could be applied at low concentration.

Through an extensive testing and development program carried out over several years involving both inactive and active trials a new process was developed. A comprehensive corrosion test program involving a large number of test specimens and covering all material in the reactor circuit was required to justify the process. The process was again a two stage process and was given the acronym MODIX (Mild Oxidative Decontamination with ion-exchange clean-up).

In the first-stage a dilute solution of potassium permanganate and nitric acid at a pH ~3 is circulated to leach chromium from the oxide film. The permanganate is then broken down by the injection of the second stage chemicals without the need for chemical removal. The second stage chemicals basically consist of a dilute mixture of EDTA and citric acid with a corrosion inhibitor, which remove the remaining oxide film. Finally the released activity and chemicals are removed from the circuit by ion-exchange.

The system arrangement showing decontamination of the reactor system is shown in Fig. 4. The process has been successfully performed on eight occasions giving effective

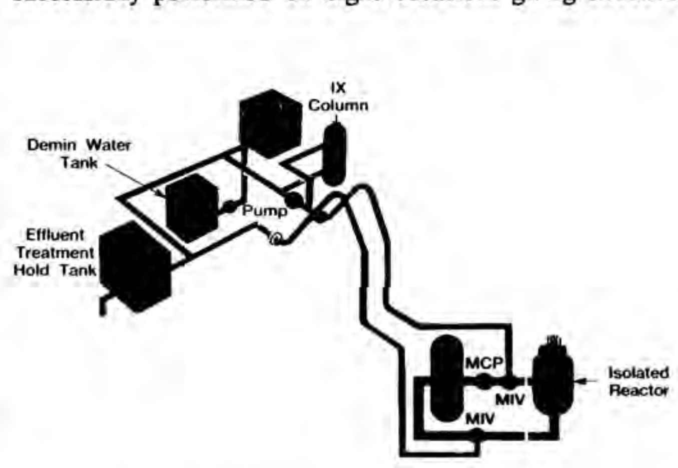


Fig. 3. Small reactor systems decontamination - Phase 1 1968-85.

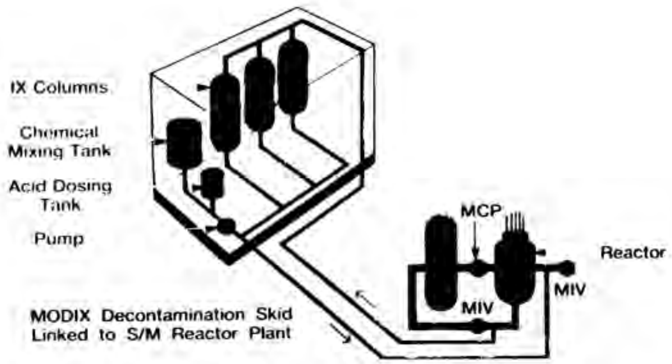


Fig. 4. Small reactor systems decontamination - Phase 2 1985 on.

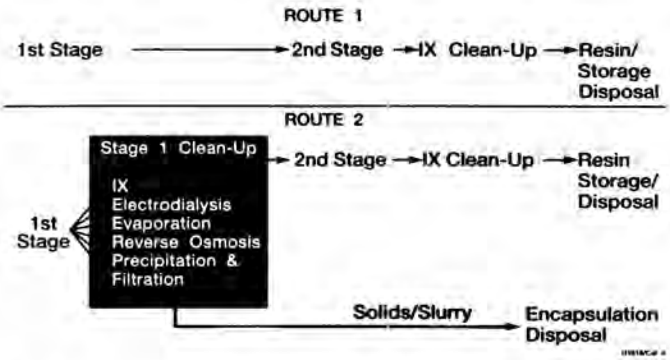


Fig. 5. Decontamination process & waste treatment options.

decontamination with DF's between 3 and 10. Multicycle applications have been carried out to achieve higher decontamination factors, to meet specific dose targets during maintenance. The benefits over the high concentration process are:

- lower fit up doses
- less recontamination in service
- lower volumes of waste

CURRENT DEVELOPMENTS WITH REGARD TO DECONTAMINATION AND DECOMMISSIONING

In-Service Decontamination

The current process based on acidified permaganate first stage is unsuitable for a mixed material plant. Development trials assessing decontamination performance and corrosion identified high concentration (1%) alkaline permaganate (AP) and ozone permanganate (03P) as the only viable alternatives. Replacements to the second stage MODIX process in combination with both AP and 03P are also being considered.

A range of options for cleaning up the circuit after the AP stage were assessed, as the previously used method, ion-exchange, would produce an excessive volume of waste arisings. The various options are shown in Fig. 5. Electrodialysis and reverse osmosis seemed highly attractive with regard to both space and energy requirements, but had to be rejected because suitable membranes to withstand the process conditions could not be identified. Precipitation and filtration was deemed impractical under the operating constraints. On the other hand, evaporative clean up using a flash evaporator seemed promising as it minimized the risks of plating out manganese dioxide. In line clean-up using a flash evaporator to minimize fouling is highly novel in reactor decontaminations. The technique is now beyond feasibility and has been fully demonstrated in rig trials. In addition vapor recompression is being incorporated for both minimizing outside steam requirements and energy savings. The waste form produced after subsequent precipitation of manganese dioxide, can be successfully encapsulated and sent for direct disposal with significant savings in storage costs. The volume to be encapsulated will be reduced by cross flow filtration of the manganese dioxide slurry using automatic membrane cleaning.

Ozone has considerable potential benefits in decontamination, since it does not add to the volume of waste produced. Significant problems in using ozone are its instability in solution, low solubility and toxicity. Considerable work has been carried out with some success in Sweden in injecting ozone solutions with various additives for decontamination of SG heads etc. (Ref 1). RRA are using a different approach in injecting ozone gas into a full pressurized circuit. This has the advantages of continuous replenishing the ozone and giving a potentially much higher ozone content. Excessive oxygen in the circuit is avoided by means of a side circuit for venting and repressurizing. Ozone combined with a dilute solution of potassium permanganate has been demonstrated to lead to a good DF whilst still being relatively benign towards the circuit materials.

An 03P/process is deemed to give a less complex plant with a higher DF and lower waste arisings, whilst the AP/process has a more established pedigree and fewer technical problems apart from the novel evaporative clean-up.

Treatment or destruction of ion-exchange resins produced from the decontamination is another area being addressed by RRA. Techniques which totally oxidize the resins and complexing agents, such as digestion with hydrogen peroxide, have been successfully demonstrated. However, these methods are most attractive where high throughput are contemplated. For smaller waste volumes, lower energy intensive methods are being evaluated. Elution techniques seem highly promising. The complexing agents can be extracted from the resins and destroyed in solution. The activity related from the resin can be generated into a more acceptable waste form.

Decontamination for Decommissioning

Most effort in decontamination at RRA has been aimed at in-service applications. The processes developed to date could be successfully applied prior to decommissioning, but would lead to undesirable wastes containing significant quantities of complexing agents. Alternatives such as mineral acids can be applied, but these remove large quantities of material from the plant, as well as requiring high concentration, with a consequent high waste loading.

Consequently a process which does not contain complexing agents and is effective at low concentration is desired. Ozone-based processes seem to be prime candidates and are being investigated by RRA. An important factor could be their ability to remove activity, unlike AP or NP. For ozone-based processes the benefits of high pressure applications are likely to be even more pronounced when corrosion of the base metal is not such a serious problem, since the cycle times can be greatly extended. In addition the processes can be applied at much lower pH, leading to higher efficiency. Alternative additives are also being considered to improve process performance.

SUMMARY

The MODIX decontamination process in conjunction with dose planning using computer codes, such as DYDAS-DOMAIN, has proved an effective tool in minimizing operator dose during planned maintenance. MODIX has been fully justified. A new process based on either alkaline permanganate or ozone-permanganate is being developed, which can be used on mixed material plants. Emphasis is now being placed on both minimizing and producing more acceptable wastes in concert with the development of the decontamination process.

For decontamination prior to decommissioning processes developed for in- service decontamination, after adaption to the different constraints, are being considered. The computer code DYDAS-DOMAIN is already in a form suitable for application in decommissioning planning.

REFERENCES

1. EP87-39 - PWR Decontamination Solvent Feasibility. Ozone Process Evaluation. May 1990.