STATUS OF SODIUM REMOVAL AND COMPONENT DECONTAMINATION TECHNOLOGY IN THE SNR PROGRAMME

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Summary

This paper summarizes the experience with sodium removal and component decontamination processes within the framework of the SNR project since the IAEA Specialists' Meeting on "Decontamination of Plant Components from Sodium and Radioactivity" at Dounreay, April 9 - 12, 1973.

The moist nitrogen process has been successfully applied to remove sodium from all 66 fuel elements of the KNK I core.

Progress has been obtained in removing sodium from fuel elements and large components by vacuum distillation.

Areas where future development is required are identified.

1. Introduction

The sodium cooled fast breeder reactor SNR 300 is under construction on the site near Kalkar at the Lower Rhine since April 1973. A supporting research and development programme is being performed by the three partners of the project in Belgium, Germany and the Netherlands. Several large sodium test facilities are operated within the framework of the SNR project, e.g. the 20 MWe Nuclear Power Plant (KNK) at Karlsruhe, Germany, the 50 MW Sodium Component Test Facility at Hengelo, The Netherlands, and the Facilities for Tests on Sodium Pumps and Handling Mechanisms at Bensberg, Germany, with sodium inventories of about 100 tons; additionally, some 30 smaller sodium test facilities are in operation in the three participating countries.

Components and test specimens exposed to non-radioactive or radioactive sodium in these facilities are cleaned by alcohol, steam, moist nitrogen, or vacuum distillation, and decontaminated, if required.

A description of our cleaning methods and our experiences gained until 1973 were presented at the Specialists' Meeting on Decontamination of Plant Components from Sodium and Radioactivity in Dounreay, April 9 - 12, 1973 [1]. The same methods are applied at present too, but they have been improved systematically since that time.

This paper covers in a condensed manner the experiences of the SNR-project partners on the areas of sodium removal and component decontamination not heretofore reported; further details will be given in separate papers at this meeting [2] to [8].

2. Requirements for Sodium Removal and Decontamination

Sodium removal and decontamination of sodium-wetted components are required for several reasons, e.g.

- to protect the maintaining personnel from chemical reactions of sodium and radiation,
- to make inspections, examinations, maintenance,and repair work possible without hindrance or danger,
- to avoid corrosion damage by sodium reaction products (especially sodium hydroxide) after re-use of cleaned components,
- to avoid pollution of the environment due to disposal or scrapping of sodium-wetted components.

Firm specified requirements have been established only in a few cases in the SNR project for cleaning sodium-wetted components:

- for spent fuel element subassemblies prior to storage and reprocessing,
- for components not intended for re-use prior to scrapping or final disposal.

The need to clean sodium components or systems has to be considered very carefully in each case; cleaning could be required for instance in the following cases:

- periodic inspections (after termination of a test or after a fixed time of operation),
- modifications or repairs,
- restoration of the required effectivness (e.g. of plugged primary cold traps, sodium vapour filters, pipings etc.),
- cleaning of spent fuel element assemblies prior to shipment for reprocessing.

There are,on the other hand,situations where cleaning components brings rather disadvantages and where certain cleaning operations cannot be applied, e.g. moist nitrogen cleaning of highly stressed or sensitized materials, vacuum cleaning of defective steam generators containing large amounts of sodium hydroxide from sodium-water reaction.

A proper design can help to make cleaning operations simpler to perform,or make a specific cleaning procedure possible at all, especially by

- partial disassembly of components or systems,
- isolation of components or systems for in-situ cleaning,
- complete drainability of sodium,
- design of components for sodium removal by vacuum distillation.

3. Sodium Removal Techniques

3.1 Alcohol

In the SNR project cleaning by alcohol is preferably used to clean small components which must be available again after a short time. This includes gripping tools to handle core internals, sodium sampling vessels, bellows valves up to internal diameters of NW 20, etc. Samples accumulating from sodium corrosion loops are also cleaned by alcohol prior to metallographic examination. In most cases, methanol (e.g. in KNK) and ethanol is used (e.g.

at INTERATOM) and, on a smaller scale, i-propanol and a mixture of i-propanol and water (5 %). Cleaning by alcohol is always supplemented by subsequent rinsing in water.

The KNK facility has a mobile alcohol cleaning cell with 2 steel tanks of 50 l capacity each in which both radioactive and non-radioactive components are cleaned. Solid carbon dioxide ("dry ice") is added to remove the heat of reaction and to precool the alcohol, respectively. In addition, the two tanks can be inertized by nitrogen. So far, more than 300 cleaning campaigns have been carried out, including 100 on the sodium sampling vessel, without ever causing secondary damage.

The same experience is available from the other partners in the project. Sodium sampling devices ("TNO harps") in the experimental loops of INTERATOM have been cleaned in alcohol for the past seven years. The sodium receiver of this device with approx. 250 g of sodium is separated from the rinsing chamber with the crucibles by a bellows valve. Temperatures during sampling may rise up to 650°C. So far, the 15 sampling systems have been cleaned for a total of approx. 300 times. After cleaning the unit is subjected to a helium leak test. If leak rates exceed 10^{-3} Torr l/s, normally the bellows valve is leaking and will be replaced. On the average a valve must be replaced after 30 cleanings.

The presence of a substoichiometric grey modification of sodium oxide, which is pyrophoric, constitutes a hazard. Preliminary treatment of alcohol in dry ice is necessary to prevent ignition. The alcohol method has so far been used to clean large components in only one special case, the removal of sodium from a defective KNK steam generator. No regeneration of the spent alcoholic solutions is planned.

In our opinion, safety aspects in handling large quantities of alcohol and the need to reprocess large quantities of sodium alcoholate are reasons to forgo this method to clean large components.

3.3 Steam or Moist Nitrogen

The moist nitrogen process has been selected as the reference method for cleaning sodium-wetted components of the SNR 300. The cleaning facilities of the SNR 300 and of INTERATOM are described in detail elsewhere [1],4.

An essential improvement in cleaning components having complicated geometries could be obtained by the use of a rotary assembling plate [9] installed in the cleaning tank. During the cleaning process, the plate rotates at a speed of 2 r.p.m. In this manner, bellows valves, plugging meters, and small cold traps have been successfully cleaned in a very short time (2.5 hrs.).

More than 100 cleaning processes have so far been carried out in the INTERATOM moist nitrogen cleaning facility; among others were two start-up cold traps of the KNK reactor, each with more than 50 kg of sodium, the prototype cold trap of the SNR 300 with a volume of approximately 1.8 m^3, 20 cold traps and 15 sodium vapour traps from INTERATOM test facilities, absorber rods, tanks, pipings, and electro-magnetic pumps. Cold traps, vapour traps, tanks, and pipings were subjected to repeated cleanings and re-uses, without any damage.

In the KNK facility medium sized or large components are cleaned by the moist nitrogen method. More than 500 washing processes have so far been carried out in this system, 150 of them on components from the radioactive primary circuit. The system and the method are described elsewhere [9]. Up to 24 kg of sodium have so far been removed per washing step. Candle filters made of sintered metal in the offgas stream tended to plug up very quickly and had to be replaced after every 10 washing processes. Washing components from the radioactive primary circuit continuously added to the contamination in the washing system and in some points led to dose rates of 2.3 rems/h caused by ^{60}Co and ^{54}Mn. Attempts for decontamination have hardly been successful so far.

Cleaning only by means of steam, used to be done formerly, is now carried out in only a few exceptional cases because of the environmental pollution it entails and the stringent requirements cleaned components must satisfy with respect to re-use.

In our experience, components exposed to sodium in radioactive and non-radioactive circuits can be cleaned rapidly and safely by the moist nitrogen cleaning method. Caustic corrosion determined in laboratory experiments or stress corrosion cracking of steels has not been observed in the practical application of this method. According to our results it is neither necessary to decrease the steam temperature below $100^{\circ}C$ to avoid damage by corrosion, nor should it be attempted, because of the considerable extension of cleaning time it would mean.

3.3 Vacuum Distillation

The SNR 300 cleaning facility is equipped for vacuum distillation cleaning of shut-down assemblies and small plant components.

In the INTERATOM test facilities, in situ distillation is used for cleaning of fuel element dummies and absorber rods. Typical cleaning conditions are 0.3 - 1 Torr at $580^{\circ}C$ and 10 hrs. cleaning time.

For the cleaning of fuel elements a modified distillation procedure was developed by INTERATOM. The fuel elements are inserted in a gas cooled vessel. When the gas cooling is interrupted, the decay heat will cause the temperature of the elements to rise. After a temperature of $550^{\circ}C$ is reached, the vessel is evacuated to evaporate the sodium adhering to the fuel elements. The gas cooling is swiched on again as soon as the maximum allowable temperature is reached. The first test results are reported in the paper of Haubold, Jansing and Kirchner [6].

Since the Specialists' Meeting in Dounreay (1973) considerable progress was made with the application of the vacuum distillation method to large components. In the TNO - 50 MW test facility at Hengelo, two steam generators and other equipment were cleaned in situ with excellent results; one of them, a 50 MW prototype evaporator, was returned to service after cleaning and has since been operating for 7000 hrs. A modified distillation procedure is being developed for the cleaning of a 85 MW-IHX tested at the Hengelo facility. Recent developments and cleaning experiences are reported by Smit in a separate paper [2].

The results of many successful cleaning operations prove that vacuum distillation is a very attractive and suitable cleaning method for small plant components. In fact it seems to be the only method that guarantees complete removal of sodium from long narrow gaps and bolted joints. The advantages are greatest when the distillation method can be performed in situ; when the intrusion of air into the component is precluded, excellent cleaning quality can be achieved. The application to large components is limited to components that are not or only slightly polluted by reaction products. For SNR 300 steam generators and IHX's the distillation method is considered as a possible alternative of the moist nitrogen method.

3.4 Requalification

In many cases, the best way to enable the requalification of a cleaned component will be to dismantle completely and to clean all parts as they are disassembled. In this way a thorough inspection is possible and highly stressed and other items sensitive to corrosion can be replaced, if necessary. Where this policy can not be followed, the cleaning procedure should be specified in such a manner that safe and reproducible results can be guaranteed. The only alternative to this policy would be to perform the necessary inspections or repair actions in an inert atmosphere and to forgo the cleaning altogether.

4. Decontamination Experience

The KNK facility has so far been operated without any failed fuel elements. Hence, only the behavior of corrosion products in the primary circuit of the plant has so far been studied. This was done by the operator and by research teams within the framework of specific experimental programs. Corrosion products so far determined in KNK primary sodium, arranged by rising concentrations, have been ^{124}Sb, ^{60}Co, ^{182}Ta, ^{54}Mn, ^{65}Zn and ^{110m}Ag. After removal of the valve plates of all check valves and control valves of the primary circuit accumulations of ^{65}Zn and ^{110m}Ag were found [10]. Similar results were obtained on specimens which had been exposed in primary sampling vessels in the KNK facility at various times and various temperatures [11]. Because of the short full power period of operation of the KNK I core (approx. 6 months) it was not necessary during the conversion phase of KNK I into KNK II to carry out further decontamination measures on the converted components after removal of the sodium. At the Karlsruhe Nuclear Research Center various decontaminating agents, such as hydrochloric acid, nitric acid with and without hydrofluoric acid, and commercial products with oxalates and citrates, have been tested on material samples from sodium in-pile loops. Various fission product nuclides such as ^{137}Cs and ^{134}Cs, have not been completely removed from the surface [5].

Moreover, the decontamination of nuclear components by molten salts and paste type cleaners has been studied in an attempt to reduce the amount of radioactive waste produced [5].

In the period December 1974 to February 1975 the KNK I core (66 fuel assemblies = 2904 fuel rods) was unloaded with a burnup between 4000 and 7000 MWd/te and cleaned by the moist nitrogen method. There was no fuel damage during the washing process. The radionuclides detected in the washing water, arranged by decreasing order of concentration, were ^{181}Ta, ^{58}Co, ^{60}Co, ^{51}Cr, ^{65}Zn, ^{51}Fe and $^{95}Zr/^{95}Nb$. Except for ^{65}Zn, these corrosion and activation products had grain sizes in excess of 0.45 μm. This method is also used to clean undamaged spent KNK II fuel elements. A change in the method, or the choice of a different method, will be necessary to clean failed KNK II fuel elements.

In the KNK facility a loaded cold trap from the radioactive primary circuit is just about to be cleaned and requalified [4].

6. Areas where Future Development is Required

6.1 General Remarks

Requalification criteria regarding the re-use of cleaned components should be established which can be likewise accepted by manufacturers, operators, and licensing authorities.

Better knowledge is required relative to the influence of reaction products remained in crevices and micropores of cleaned components on the corrosion behaviour after re-use in sodium systems, and during storage in air or inert gas, in relation to the applied cleaning procedure, respectively.

6.2 Sodium Removal

The applicability of the moist nitrogen cleaning process is highly influenced by the corrosion behaviour of the sodium-wetted components during the cleaning procedure. Better knowledge is needed on the corrosion behaviour of the various materials during the cleaning process in consideration of the antecedent exposure to liquid sodium (time, temperature, sodium impurities, mechanical stresses, sensitized condition etc.), and of the cleaning conditions (time, temperature, sodium hydroxide concentration on the surface, steam concentration).

The applicability of the vacuum distillation cleaning process can be better estimated if better knowledge is available on the following areas:

- Corrosive effects of sodium hydroxide and sodium oxide during the distillation procedure as a function of temperature, time, surface concentration, and material,
- Provisions required for vacuum distillation cleaning of large components and systems in situ.

6.3 Decontamination

The efficiency of decontamination procedures can be highly improved if better knowledge is gained by the following actions:

- Investigations on the influence of various decontamination agents on the corrosion behaviour of various materials during the decontamination process in consideration of the antecedent exposure to liquid sodium (see 6.2).
- Development and testing of procedures for cleaning and decontamination of spent primary cold traps considering the problems of volatile radionuclides (tritium, caesium),
- Development and testing of procedures to convert the content of spent primary cold traps to substances suited for final storage,
- Development and testing of procedures to remove radionuclides from primary sodium (e.g. from cold traps, large leakages, reactors) for re-use.

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