IAEA-TECDOC-1022

New methods and techniques for decontamination in maintenance or decommissioning operations

Results of a co-ordinated research programme
1994–1998

INTERNATIONAL ATOMIC ENERGY AGENCY

The originating Section of this publication in the IAEA was

Waste Technology Section
International Atomic Energy Agency
Wagramer Strasse 5
P O Box 100
A-1400 Vienna, Austria

NEW METHODS AND TECHNIQUES FOR DECONTAMINATION
IN MAINTENANCE OR DECOMMISSIONING OPERATIONS
IAEA, VIENNA, 1998
IAEA-TECDOC-1022
ISSN 1011-4289

Printed by the IAEA in Austria
June 1998

FOREWORD

Decontamination of nuclear facilities is a subject of increasing importance as the nuclear community considers the issues related to the decommissioning of surplus or obsolete facilities and making modifications to operational facilities, or conducts the necessary inspections and maintenance to permit continued efficient and safe operation of existing facilities. The IAEA has responded to the needs of its Member States in this area by facilitating the dissemination and exchange of current technology and by supporting programmes which conduct research and development aimed at furthering the related technologies.

Previous co-ordinated research programmes (CRP) conducted respectively from 1984 to 1987, and from 1989 to 1993, highlighted the role of decontamination within the overall domain of decommissioning. However, subjects such as decommissioning project management, dismantling techniques and radiological characterization were also a significant part of those programmes. With technological progress, it became clear that decontamination had developed to the point of being a scientific and technical discipline per se, and required a straightforward, specialized approach, including related research and development activities. For example, selection of a decontamination technique is a complex process in that several criteria are supposed to be met, such as adequate decontamination factors, acceptable corrosion rates, ready availability of the equipment, simple operation and control, acceptable costs of application and minimal amounts of waste. Having recognized technological progress in decontamination and the large potential for optimization, the CRP on New Methods and Techniques for Optimization of Decontamination for Maintenance or Decommissioning was launched and conducted by the IAEA from 1994 to 1998.

Concluding reports that summarized the work undertaken under the aegis of the CRP were presented at the third and final Research Co-ordination Meeting (RCM) held in Mol, Belgium, 12–16 January 1998 and are collected in this Technical Document. Operating experience in real-scale applications, lessons learned, key results in laboratory scale or pilot scale research, and validation of mathematical models, are among the most significant achievements of the CRP and have been highlighted. The IAEA officers responsible for the CRP were J. Wiley (first RCM) and D. Clark (second and third RCMs and compilation of the report) both of the Division of Nuclear Fuel Cycle and Waste Technology. The IAEA wishes to express its thanks to all the participants in the programme and would like to take this opportunity to acknowledge the co-operation and warm hospitality of the institutes that hosted the RCMs.

CONTENTS

SUMMARY OF THE CO-ORDINATED RESEARCH PROGRAMME

1. BACKGROUND

The International Atomic Energy Agency first introduced the subject of decontamination and decommissioning into its programme in 1973, publishing reports reflecting the needs of its Member States on these topics. These reports (see Table I) summarize the work done by various Technical Committees, Advisory Groups and International Symposia.

The decontamination and decommissioning of nuclear facilities is of great interest to many Member States of the IAEA because of the large number of older nuclear facilities which have been, or soon will be, retired from service. In response to increased international interest in this area and to the needs of Member States, the IAEA initiated in the 1980s the Co-ordinated Research Programme (CRP) on Decontamination and Decommissioning of Nuclear Facilities to create a forum for scientists from different Member States, to bring them into closer contact.

The first phase of the CRP was carried out from 1984 to 1987. The scope of the programme was mainly oriented towards decontamination. However, selected decommissioning projects were included so that the participants could see how their work related to overall decommissioning activities. The salient features and achievements of the co-ordinated research work performed were summarized in IAEA-TECDOC-511 (1989). It was the recommendation of the participants that the IAEA should extend such initiative and undertake another phase of the CRP on decontamination and decommissioning.

In line with the recommendation of the experts who participated in the first phase of the CRP, the aim of the second phase was to include several areas of decontamination and decommissioning. It was also suggested that the number of participants should be increased to include participation from other Member States, especially from developing countries. The second phase of the CRP was established in 1989 and concluded in 1993. Research co-ordination meetings (RCMs) were held in Vienna (1989, 1991) and in Japan (1993). IAEA-TECDOC-716 (1993) summarizes CRP results and conclusions.

The experience of the past CRP on decontamination and decommissioning has highlighted the difference between these two subjects, covered previously under a common programme. In particular, decommissioning is a problem where many disciplines are involved, such as radiation protection, waste management, chemical and mechanical engineering, electronics/robotics, dismantling technology, planning, economics and decontamination. The technical staff involved in decontamination may not need to be entirely familiar with other disciplines and vice versa. Therefore, a specialist's approach to decontamination must be pursued. As an independent discipline, decontamination technology has many areas of application for a nuclear installation. Decommissioning is only one such area; other areas include operation, maintenance, inspection, refurbishment and plant life extension.

In general terms, decontamination for decommissioning purposes may use 'aggressive' techniques to achieve high decontamination efficiency, since maintaining integrity and operability of the decontaminated components is not required. This philosophy may be somewhat true for refurbishment and plant life extension where old decontaminated components are replaced by new ones. On the other hand, decontamination for maintenance, and to a great extent for operation and inspection purposes, must maintain integrity and operability of the decontaminated components. Hence, relatively 'mild' techniques may be used in these cases to achieve optimum decontamination efficiency.

In view of the progressive ageing of nuclear installations operating worldwide and the buildup of radioactive contamination, decontamination is increasingly needed to reduce doses to workers engaged in maintenance activities. Components may have to be repaired or dismantled and removed. All of these activities considerably impact on occupational exposures. Also, a growing number of nuclear installations are permanently shut down, and hence become candidates for decommissioning. In decommissioning, decontamination may have the additional objective of reducing the residual radiation source at the site in preparation for protective storage or permanent disposal work. Another important objective would be to salvage equipment and materials and restore the site and facility, or parts thereof, to an unrestricted use condition.

While the basic technology necessary for accomplishing decontamination is reasonably well developed, there are still several areas worthy of further studies and optimization. Decontamination is a complex process that should meet several criteria, such as adequate decontamination factors, acceptable corrosion rates, easy availability of the equipment, simple operation and control, acceptable time requirements, satisfactory safety aspects (both radiological and non-radiological), acceptable costs of application and minimal amounts of wastes. A rapid exchange of information and co-ordination of work are required to foster technology, reduce duplication of efforts and provide useful results for those Member States planning decontamination activities.

In view of the large number of aging or shutdown nuclear installations and the assurance of safety and radiation protection that the decontamination technology provides to plant workers and to the public, the IAEA considered appropriate to encourage R&D work on decontamination and launched in 1994 a CRP on New Methods and Techniques for Optimization of Decontamination for Maintenance or Decommissioning. Ten Research Agreements and three Research Contracts were included in this CRP. Under the aegis of this CRP, three Research Co-ordination Meetings (RCM) were held, respectively, in Vienna (31 October-4 November 1994), Mumbai , India (26 February –1 March 1996) and finally Mol, Belgium (12-16 January 1998). This TECDOC includes final project reports presented at the Mol meeting.

This publication is mainly intended as a first-hand tool for scientists responsible for R&D programmes in decontamination. Practical results of decontamination research should also be of interest to operators of nuclear facilities, including those involved in plant decommissioning. Contractors and suppliers of specialized services should also be interested as decontamination is a preparatory step to activities such as inspection, maintenance, disassembly and demolition of components/structures.

TABLE I
LIST OF IAEA PUBLICATIONS ISSUED SINCE 1980 ON DECOMMISSIONING AND DECONTAMINATION OF NUCLEAR FACILITIES

	Safety Series	
1.	Factors Relevant to the Decommissioning of Land-Based Nuclear Reactor Plants	No. 52 (1980)
2.	Safety in Decommissioning of Research Reactors	No. 74 (1986)
3.	Regulatory Process for the Decommissioning of Nuclear Facilities	No. 105 (1990)
	Technical Reports Series	
1.	Decommissioning of Nuclear Facilities: Decontamination, Disassembly and Waste Management	No. 230 (1983)
2.	Decontamination of Nuclear Facilities to Permit Operation, Inspection, Maintenance, Modification or Plant Decommissioning	No. 249 (1985)
3.	Methodology and Technology of Decommissioning Nuclear Facilities	No. 267 (1986)
4.	Methods for Reducing Occupational Exposure During the Decommissioning of Nuclear Facilities	No. 278 (1987)
5.	Decontamination and Demolition of Concrete and Metal Structures During the Decommissioning of Nuclear Installations	No. 286 (1988)
6.	Factors Relevant to the Recycling or Reuse of Components Arising from the Decommissioning and Refurbishment of Nuclear Facilities	No. 293 (1989)
7.	Monitoring Programmes for Unrestricted Release Related to Decommissioning of Nuclear Facilities	No. 334 (1992)
8.	Cleanup and Decommissioning of a Nuclear Reactor After a Severe Accident	No. 346 (1992)
9.	Application of Remotely Operated Handling Equipment in the Decommissioning of Nuclear Facilities	No. 348 (1993)
10.	Planning and Management for the Decommissioning of Research Reactors and Other Small Nuclear Facilities	No. 351 (1993)
11.	Decontamination of Water Cooled Reactors	No. 365 (1994)
12.	Decommissioning Techniques for Research Reactors	No. 373 (1994)
13.	Safe Enclosure of Shutdown Nuclear Installations	No. 375 (1995)
14.	Design and Construction of Nuclear Power Plants to Facilitate Decommissioning	No. 382 (1997)
	Technical Documents (TECDOC)	
1.	Decontamination of Operational Nuclear Power Plants	IAEA-TECDOC-248 (1981)
2.	Decontamination and Decommissioning of Nuclear Facilities: Final Report of Three Research Meetings (1984-87)	IAEA-TECDOC-511 (1989)
3.	Decontamination of Transport Casks and of Spent Fuel Storage Facilities	IAEA-TECDOC-556 (1990)
4.	Factors Relevant to the Sealing of Nuclear Facilities	IAEA-TECDOC-603 (1991)
5.	Considerations in the Safety Assessment of Sealed Nuclear Facilities	IAEA-TECDOC-606 (1991)
6.	National Policies and Regulations for Decommissioning Nuclear Facilities	IAEA-TECDOC-714 (1993)
7.	Decontamination and Decommissioning of Nuclear Facilities - Results of a Co-ordinated Research Programme, Phase II: 1989-1993	IAEA-TECDOC-716 (1993)
	Nuclear Data Series (NDS)	
1.	Nuclear Data Requirements for Fission Reactor Decommissioning	INDC (NDS)-269 (1993)
2.	International Benchmark Calculations of Radioactive Inventory for Fission Reactor Decommissioning	INDC (NDS)-355 (1996)

2. SUMMARY OF MAJOR TECHNICAL ACHIEVEMENTS

The CRP had the objective of exploring practically all of the aspects of decontamination ranging from theoretical modelling to laboratory, pilot or industrial scale testing applications.

Included in the scope of this CRP are the following subject areas:

(a) Characterization of surface contamination as a precursor to decontamination:
  - evaluation of radioactive inventory, its estimation and measurements;
  - extent of contamination; and
  - physico-chemical form of the contamination.

(b) Identification of the decontamination objectives and the required degree of decontamination.

(c) Factors influencing the selection of decontamination process:
  - system-related factors (e.g., material types and geometries; contamination characteristics; plant operating history; etc.);
  - agent-related factors (e.g., corrosion effects; decontamination effectiveness; solvent stability and concentration; fluid volumes generated; waste processing requirements; process duration; and
  - redistribution of contaminants; toxicities; process costs, including waste processing; etc.).

(d) Methodologies for optimization as applied to decontamination (why it is decided to decontaminate; how the selection of a decontamination process is made; etc.).

(e) Melting as a means to decontaminate metals.

(f) New developments, recent progress in decontamination.

It should be noted that practically each of the above-mentioned areas has been adressed by one or more research contracts/agreements, which has resulted in an effective coverage of decontamination as an integrated process. A complementary consideration is that some research activities concerned mainly operational facilities and the associated need to reduce radiation doses and restore more acceptable working conditions, other research activites focused on decontamination for decommissioning purposes, while a few more addressed techniques in principle applicable to a number of plant conditions and decontamination objectives. A variety of institutions have taken part in this CRP, ranging from electrical utilities to research institutes and private companies providing specialized services. From all of these viewpoints, it is possible to state that this CRP has provided a good overview of worldwide R&D activities in the decontamination field. Specific points to be highlighted based on participants' reports which are included in this document, and on informal discussions, are described below.

2.1. Nature of contamination layers

In primary reactor systems the radioactive contamination on the internal surfaces is a result of the deposition from the reactor coolant of neutron activated particles and dissolved elements and of fission products and transuranics released when there is a failure of fuel cladding. These deposits become part of the oxide layer which forms on the inside of the piping. This layer has a complex structure which depends on a variety of parameters such as coolant chemistry, temperature of formation, system materials and operating time. It is normally imperative to characterize these layers to identify the best decontamination methods to remove the surface oxides. The composition and form of these layers vary with the type of reactor, and extrapolation from one reactor to another , even of the same type, should be done very cautiously.

Several research activities under this CRP (Belarus, Hungary, India, Italy, UK) focused on characterization of contaminated layers as a precursor to decontamination. A few details might be of interest to the reader. Contamination of the Belorussian reactor is somewhat unique because of the gas mixture (N_2O_4/ NO_2) used as a coolant in that reactor. It is also interesting that the researchers found different compositions in layers affected by operational temperature lower than 100°C, 200°C or between 300-500°C. This parameter in turn oriented their decontamination trials. Mention should also be made of the UK work which is a physico-chemical model of the interactions controlling the contamination/decontamination mechanisms of uranium or plutonium-contaminated layers. Under this CRP, contamination existing in a variety of reactors has been investigated (BWR, in India and Italy; PWR in Italy; WWER in Hungary).

2.2. Chemical and electrochemical decontamination processes

It is well known that there is no universal decontaminating agent, as the performance of any given solution will depend on a number of plant-specific parameters and requirements. Each plant should select decontaminants on the basis of its own experience and needs and having taken account of advantages and inevitable drawbacks of each possible solution. As mentioned elsewhere, the decontamination factor is only one of the requirements in selecting a decontamination technique. The management of secondary wastes (e.g., spent decontaminants) is essential. It is noteworthy that several research activities under this CRP concentrated on various aspects of decontamination, including waste management. Several techniques have been tested and optimized in the following countries and are described in the relevant papers:

Belarus — acidic solutions of potassiun permanganate and others;

Belgium — the two-step CORD process and one-step processes such as a mixture of nitric and hydrofluoric acid and cerium 4+ solutions. The cerium process was eventually selected for full-scale application.

China — cerium 4+ and nitric acid solutions. This research work included the development of an electrolytic cell (regenerator) to re-oxidize cerium back to cerium 4+ and allow recycle of the decontaminant.

France — foam decontamination. This is an emerging technique having some advantages such as the use of small amounts of liquids and low generation of secondary wastes, high penetration in fissures or cracks, and possibility of recirculation and filtration.

Hungary — low concentration methods for decontamination of the full primary system. Treatment cycles included the following tests: alcaline or acidic oxidation followed by CITROX or gluconic acid washing. A significant part of this research work addressed the purification of decontamination solutions.

Indonesia — strippable coatings to decontaminate a radioisotope production hot cell for reuse, including items of various materials and the cell itself.

Italy — decontamination tests using the following chemical processes: ‘soft’ chemicals; aggressive chemicals; chemicals with ultrasounds; and electrodecontamination.

Slovakia — new chemical and electrochemical solutions to decontaminate selected equipment (steam generator, pressurizer) of Slovakia's WWER-440 and WWER-1000 reactors.

2.3. Non-chemical decontamination processes

This CRP included also several research projects involving mechanical and other decontamination techniques. They are summarized as follows:

Belgium — wet abrasive cleaning methods. Different abrasives were tested.
Canada — decontamination of tritium- contaminated surfaces at the Darlington Tritium Removal Facility. In this case, ultraviolet radiation and ozone gas were successfully used to decontaminate stainless steel materials, with much poorer results for non-metallic surfaces.
Germany — melting facility to decontaminate and recycle metals contaminated by the Chernobyl accident.The melting technology has been successfully implemented in Germany for decades to decontaminate metal parts from decommissioned installations. The project reported in this CRP is related to a particularly challenging application.
The Netherlands — separation of radioactive concrete constituents. This emerging technology is based on a different contamination distribution between concrete constituents. Basically contamination penetrates the porous concrete stone, while dense aggregates like granite and limestone are relatively immune from contamination. Separation of concrete constituents would then entail a significant reduction of radioactive waste volumes. This project aimed at the optimization of a test separation plant.

3. CONCLUSIONS

Over the course of this CRP, considerable progress has been made in all of the research projects, and the sharing of pertinent experience and information has been timely and beneficial to all parties. The participants all agreed that the programme was of real value to them, both in terms of understanding the various investigations/accomplishments and of planning or implementing subsequent activities. It was generally agreed that decontamination of metals (e.g., with chemicals, wet/dry blasting, and melting) is well developed for decommissioning applications. However, this is not the case for concrete wastes from decommissioning. In this context, a need for further research in the following areas has been identified:

(1) Characterization methods for contaminated concrete.
(2) Decontamination methods for concrete which would result in lower doses for the workers.
(3) Improvements in volume reduction for secondary wastes from decontamination (in particular, of concrete).

There are no generally applicable decontamination methods for metals for reducing dose during operations and maintenance. Plant specific issues include waste volumes, corrosion of metal surfaces, decontamination factor requirements, and qualification plans. The susceptibility of materials to recontamination following decontamination is an important factor to consider when selecting a process for operation and maintenance activities.

There is clearly a desire for individual Member States to develop self-reliant technologies for full system decontamination. In part, this is due to the need to understand the effects of the decontamination under site specific conditions in order to satisfy the nuclear regulators, but also due to fact that many available processes are proprietary formulations. In some Member States, it is very difficult to implement full system decontamination for these reasons and the costs associated with such a project are relatively high. Other areas of concern that emerged from experts' discussions and their papers are the following:

- Decontamination and decommissioning of plant system components should be considered at the plant design stage.
- ALARA principles should be applied more effectively in decontamination efforts.
- There is need for the harmonization and rationalization of unrestricted release criteria among various Member States. As a comment, it may be stated that this effort is being done under the auspices of the IAEA.
- There is need for a similar rationalization for qualifying processes for the decontamination of entire systems. It is recognized that specific plants may have unique characteristics that need to be considered when a decontamination process is qualified for that particular plant, nevertheless it is necessary for each plant operator to consider a common set of questions when planning a qualification plan. The development of these common questions and principal considerations for applying decontamination processes to various plants remains as an important technical challenge.

DECONTAMINATION AS A PART OF DECOMMISSIONING AND MAINTENANCE WORK AT NUCLEAR INSTALLATIONS

V.M. EFREMENKOV, N.I. VORONIK, N.V. SHATILO
Research and Technical Centre 'Sosny',
Academy of Sciences,
Belarus

XA9847481

Abstract

The purpose of the work was to check applicability of the existing and new compositions for decontamination and their adjustment to the specific conditions dealing with operation of the research reactor with N_2O_4/NO_2 cooling system.

Determining factor in selection of decontamination solution was the work temperature of installation, because chemical and phase composition of corrosion product deposits on the surfaces to be decontaminated depends namely on temperature.

Investigations of corrosion resistance of construction materials in tested decontamination solutions showed the absence of general, contact, aperture and intercrystallite corrosion.

INTRODUCTION

The Institute of Nuclear Power Engineering during several years developed a mobile version of a nuclear power plant with gaseous N_2O_4 as coolant agent and working fluid for the turbine. Now that this programme has been stopped, the reactor and all supporting systems dismantled, the problem was to decontaminate some equipment and valuable materials for their re-use and for facilitating further dismantling of heavily contaminated components of the primary reactor circuit. Since N_2O_4 is a very chemically aggressive gas, especially in the presence of any small amounts of water or water vapour, some parts of the coolant system, pipelines, reactor vessel, etc. have been corroded. Radioactive contaminants, mainly activated isotopes of some elements, are present in very small amounts in the coolant system, concentrated mainly in the oxide film (corrosion products), formed on the affected surfaces.

In practice of decontamination of nuclear installations both for maintenance and decommissioning a lot of experience has been collected. Rather wide range of decontamination techniques and compositions have been described in the literature for decontamination of water cooled reactors and associated equipment. The specific feature of our work deals with specific properties of the coolant system of our experimental reactor, namely dissociating gas N_2O_4/NO_2. Both in water coolant system and in N_2O_4/NO_2 atmosphere corrosion of the construction materials leads to the formation of corrosion products, and the objective of decontamination is mainly to dissolve or delete in the other way the corrosion films with incorporated fission and activated corrosion products. However the structure and composition of these corrosion products in these cases may be quite different, which request different approaches and different compositions for decontamination. The purpose of the work was to check applicability of the existing compositions for decontamination and their adjustment to the specific conditions, dealing with operation of the reactor with N_2O_4/NO_2 cooling system.

BACKGROUND INFORMATION

It is known that the choice of a decontamination method is basically determined by the following major considerations:

- the nature of radionuclides to be removed: type, physical and chemical forms;
- the nature of the material to be decontaminated, existence and structure of corrosion products;
- the level of decontamination to be reached;
- the fate of decontamination material:
  - declassification,
  - recycling and re-use;
  - disposal as waste;
- the location of the decontamination operation;
- the nature, quantity and treatment of secondary waste;
- the safety of operation;
- the economic balance of operation.

Effectiveness of decontamination depends on character of sorption of radioactive impurities, nature of sorption surface and properties of oxides formed. In our case selection of decontamination composition was defined by the nature of the material to be decontaminated (mainly stainless steel of different composition), the composition of oxides on the contaminated surface (which was quite different depending on the conditions of operation), and the fate of the materials to be decontaminated (decontamination for unrestricted release).

Decontamination of steel practically always involves dissolution/deleting of oxides and other corrosion products from the surface of metal. For an oxide to be dissolved, two conditions must be met. First, there must be a thermodynamic driving force and, second, a kinetic pathway must be available for the transfer of components into solution. The first of these conditions is easier to achieve than the second.

The most obvious method of destabilising the oxide lattice is to attack the oxide sub-lattice with protons:

$$\underset{\text{acid}}{8\,H^+} + \underset{\text{oxide}}{Fe_3O_4} \rightarrow \underset{\text{metal ions in solution}}{Fe^{+2} + 2\,Fe^{+3}} + 4\,H_2O$$

This is the basis of decontamination methods based on use of mineral or organic acids. However, acid attack is slow for many types of oxides unless the reagents are used at high concentrations.

Since attack on some oxides by protons alone requires concentrated reagents, an alternative approach is required with diluted reagents. Attack on the cation sub-lattice by electrons provides a method of achieving rapid dissolution.

$$\underset{\text{acid}}{8\ H^+} + \underset{\substack{\text{reducing}\\\text{agent}}}{2\ e^-} + \underset{\text{oxide}}{Fe_3O_4} \rightarrow \underset{\substack{\text{metal ions}\\\text{in solution}}}{3\ Fe^{+2}} + 4\ H_2O$$

The overall reductive-dissolution reaction can be broken down into two steps:

- The first one is the transfer of an electron from the reducing agent to the oxide's metal ion to produce an unstable reduced species.
- The second one is the removal of this reduced ion and associated oxide anions into solution.

In order to increase metal-ion solubility at pH's approaching neutrality, a complexing agent may be added to the solution.

There are three conditions that a reductive-dissolving agent must fulfil:

a) rapid electron-transfer mechanism;

b) chelation to provide adequate metal-ion solubility;

c) sufficient proton concentration to give rapid dissolution of oxide anions.

Oxidative methods depends on the oxidation of Cr (III) to Cr(IV), which then dissolves as chromate to leave a residual iron-rich oxide. This can be done in acid or alkaline solutions, and the Red-Ox potential of the metal depends on the pH.

$$Cr_2O_7^{-2} + 14\ H^+ + 6\ e^- \xrightarrow[\text{ox}]{\text{red}} 2\ Cr^{+3} + 7\ H_2O$$

$$CrO_4^{-2} + 4\ H_2O + 3\ e^- \xrightarrow[\text{ox}]{\text{red}} Cr(OH)_3 + 5\ OH^-$$

Historically, interest has concentrated almost exclusively on one reagent for this oxidation – alkaline potassium permanganate (AP). The overall stoichiometry of the reaction of Cr (III) oxides and alkaline $KMnO_4$ can be described with reference to Cr_2O_3

$$Cr_2O_3 + 2\ MnO_4 + 2\ OH^- \rightarrow 2\ CrO_4^{-2} + 2\ MnO_2\downarrow + H_2O$$

The precise mechanism of the oxidation reaction is not well understood. However, other metal ions that are normally present in oxide layer (Fe or Ni) are not soluble under alkaline conditions. Thus the reagents work by leaching chromium from the oxide layer, leaving behind a coating of chromium-depleted oxide plus MnO_2. These are removed in a second treatment, with acid and/or chelating reagents.

As it is known, alkaline permanganate is effective on many reactor oxides, even with relatively low concentration of $KMnO_4$ and NaOH. A variation of this approach is to use permanganate, at low concentration, in acid solution. This is generally more effective on stainless steel oxides that the alkaline reagent, and also leads to lower waste volumes.

In our work specifically it was necessary to decontaminate the elements of low and high pressure turbines and some other equipment of the experimental reactor.

The equipment to be decontaminated was operated in the atmosphere of N_2O_4/NO_2 in wide range of temperature (50 - 450°C) and pressure 0.8 - 4.4 MPa. All surfaces to be decontaminated have corrosion films of different thickness and composition. Surface of the equipment which worked at low temperature and pressure had relatively friable corrosion products.

The main components of corrosion deposits are combinations of Fe, Cr and Ni in oxides and nitrates forms.

Comparative chemical and phase compositions of deposits at working surfaces of installations with heating mediums H_2O and N_2O_4 are presented in Table 1.

TABLE 1. CHEMICAL AND PHASE COMPOSITIONS OF DEPOSITS

N_2O_4			H_2O		
Main chemical composition, %		Phase composition	Main chemical composition, %		Phase composition
Fe	2-20	$(NO)_n[Me(NO_3)_m]$	Fe	45-74	γ Fe_2O_3
Cr	1-10	$NiFe_2O_4$	Cr	0.1-1.8	α Fe_2O_3
Ni	1-7	$NiCr_2O_4$	Ni	0.01-1.8	Fe_3O_4
Si	0.5-9	$Fe_2O_3 \cdot Cr_2O_3$	Si	0-1.6	FeOOH
Mg	0.1-1.2	α Fe_2O_3	Mg	0.01-1.7	
Al	0.02-1.3		Cu	0.1-0.4	
			Zr	0.1-0.2	

Before starting decontamination of real contaminated equipment the attention was paid to the differences in compositions and structure of corrosion products at the surface of simulated samples and the surfaces of real equipment. Conditions for corrosion products formation in these two cases were different, static conditions for simulated samples preparation, and dynamic conditions for operation of real equipment, when cooling media (N_2O_4/NO_2) was circulated together with some corrosion products. The latest was sedimented in some places to contribute to the formation of corrosion film and contamination of the surface of the equipment.

On the other hand, structure of corrosion products and associated films and sediments on the surface of equipment depends on the conditions of the equipment's operation. At high temperature ($\approx$ 450°C) and pressure (4.4 MPa) in N_2O_4/NO_2 atmosphere solid dense film of corrosion products is created, consisting mainly from Fe_2O_3, $Fe_2O_3 \cdot Cr_2O_3$, $NiCr_2O_4$. At low temperature (40-50°C) and pressure ($\approx$ 0.8 MPa) the corrosion products are rather crumbly and consist from $NiO(CrFe)_2O_3$, $NiFe_2O_4$, nitro- and nitroso-complexes of Fe, Cr and Ni.

The character of corrosion products generated on the surface of equipment defines the option of decontamination.

In quantitative relation the radionuclides are distributed in deposits by the manner:

$^{60}Co > ^{54}Mn > ^{51}Cr > ^{59}Fe > ^{58}Co$ (for N_2O_4) and $^{60}Co > ^{51}Cr > ^{58}Co \approx ^{54}Mn$ (for H_2O).

Contamination level of the equipment outside the reactor vessel was in range between $8 \cdot 10^{-2}$ and $2 \cdot 10^{-3}$ Ci / m^2.

The main purpose of this work was to develop chemical compositions for decontamination, such as equipment, which was mainly constructed using stainless steel.

Chemical compositions of some of these steels are presented in Table 2.

TABLE 2. COMPOSITIONS OF CONSTRUCTION MATERIALS (STAINLESS STEEL)

Composition of steel	C, %	Cr, %	Ni, %	Ti, %	Si, %	Mn, %	Cu, %	Fe, %
08X18H10T	0.08	18	10	0.6	0.8	2	0.3	<78
12X18H10T	0.12	18	10	0.6	0.8	2	0.3	<77
20X23H18	0.20	23	-	-	0.3	0.8	-	<75
20X13	0.20	13	-	-	-	-	-	<80
30X13	0.30	13	-	-	-	-	-	<80
14X17H2	0.14	17	2	-	0.1	-	0.02	<80
13X11H2B2	0.13	11	2	-	-	0.12	0.1	<86

ACCOMPLISHMENTS

Before starting experiments on decontamination of real equipment experiments were carried out with simulated samples of construction materials to find the most appropriate composition for decontamination. For this purpose samples of different construction materials (steels) were contaminated with radionuclides of Cr-51, Fe-59, Mn-54 and exposed in sealed ampoules to N_2O_4 at different temperature and pressure. For decontamination of such samples some simple compositions were studied using inorganic and organic acids and their salts.

Nitric, sulphuric, phosphoric, oxalic, hydrofluoric and succinic acids as well as ammonium oxalate and hydrazine sulphate were selected for testing. The experiments were carried out at different temperatures (25, 60 and 90°C) during 1, 3 and 5 hours. The decontamination factor (ratio of initial radioactivity of sample to the activity after decontamination $K = A_0/A_1$) was calculated separately for each isotope, namely ^{51}Cr, ^{59}Fe, ^{54}Mn, and then the average value was calculated. Some selected experimental results are presented in Table 3.

It was found that among inorganic acids the most effective and reasonable concentration and temperature are nitric and sulphuric acids. Hydrofluoric acid is not very effective, and hydrochloric acid is very aggressive in terms of corrosion.

TABLE 3. DECONTAMINATION OF STAINLESS STEEL SAMPLES (20 X18H10T) WITH ACIDS

Composition	T, °C	Time, hours		
		1	3	9
5% HNO_3	25	7±1	6±1	8±1
	60	20±3	30±5	30±6
	90	22±3	43±5	45±5
10% HNO_3	25	15±5	17±5	18±5
	60	22±4	30±5	35±9
	90	30±8	50±8	140±15
20% HNO_3	25	15±4	16±4	11±3
	60	30±3	64±12	53±12
	90	54±10	98±20	460±60
2% H_2SO_4	25	8±1	9±1	11±3
	60	16±2	32±5	53±12
	90	71±8	210±40	460±60
5% H_2SO_4	25	9±1	13±2	16±4
	60	20±3	62±8	89±11
	90	280±60	2100±640	-

TABLE 3. (Cont.)

Composition	T, °C	Time, hours		
		1	3	9
10% H_2SO_4	25	4±1	12±2	-
	60	21±3	65±9	-
	90	250±40	-	-
0.5% HCl	25	20±3	43±6	8±1
	60	270±90	320±80	-
	90	2300±400	-	-
2.5% H_3PO_4	25	5±1	11±2	21±3
	60	20±3	17±5	56±6
	90	40±5	96±12	-
5% H_3PO_4	60	18±2	27±5	61±7
	90	42±6	103±16	210±40
1% HF	25	41±10	60±9	77±10
5% HF	25	17±12	62±9	-
0.5% $H_2C_2O_4$	25	3±0.5	4±0.7	6±0.8
	60	31±7	60±12	80±14
	90	210±60	1100±830	-
1% $H_2C_2O_4$	25	4±0.5	6±0.8	-
	60	14±2	64±8	82±8
	90	580±150	1500±290	-
1% $(NH_4)_2C_2O_4$	25	1.2±0.1	1.4±0.1	-
	60	4.5±0.6	4.5±1.7	8.2±8.0
	90	8.1±1.0	12±2	14±2
5% $(NH_4)_2C_2O_4$	25	3.5±0.3	6.8±0.3	-
	60	17±2	80±3	22±18
	90	41±8	120±50	310±60
1.2% $N_2H_4H_2SO_4$	75	3.8±0.4	-	14±3
2% $N_2H_4H_2SO_4$	75	70±11	-	168±31

It was found out that oxalic acid even at low concentration is quite effective for decontamination and increasing of its concentration does not influence the effectiveness of decontamination. Ammonium oxalate is less effective than oxalic acid.

Low solubility of the corrosion products of stainless steels with high content of chromium in simple acidic solutions is defined by high concentration of Cr(III) oxides in corrosion film. Actually because of high diffusion rate of chromium in steel towards the border between metal and gaseous phase corrosion products became enriched by chromium during corrosion process. Preliminary experiments with solutions of simple acids have shown that these simple compositions are not effective for decontamination of stainless steel samples exposed in N_2O_4/NO_2 at high temperature and pressure. To improve effectiveness of decontamination several approaches have been tested.

The first approach was to add sorbent to the neutral or acidic decontamination solution. As a sorbent the silica gel powder with grains size of 0.2-0.5 mm was added in amount of 50 g/l to the solution of oxalic acid or solution of hydrazine sulphate. The latest was tested as a neutral solution of complexing agent. The experiments were carried out at static conditions, when the vessel with decontaminating samples, decontamination solutions and sorbent was shaken during 3 hours at the room temperature. The results of experiments are presented in Table 4.

TABLE 4. ONE STAGE DECONTAMINATION OF SIMULATED SAMPLES

Decontamination composition	Decontamination coefficient		
	Cr-51	Mn-54	Fe-59
Hydrazine sulphate*, 20 g/l (pH 1,3)	150±20	190±30	230±40
Hydrazine sulphate, 20 g/l + silica gel (pH 1,3)	470±60	580±70	1550±90
5% $(NH_4)_2C_2O_4$ (pH 6,4)	30±5	20±4	200±20
5% $(NH_4)_2C_2O_4$ + silica gel (pH 6,4)	140±40	270±40	1300±70

* Hydrazine sulphate - $N_2H_4 \cdot H_2SO_4$

It can be seen from the table that addition of the sorbent to the decontamination solution increases substantially decontamination factor, which can be explained both by mechanical impact of silica gel grains on the decontaminating surface, and by sorption on silica gel radionuclides transferred from the contaminated surface into decontamination solution. Study of radionuclides sorption on silica gel at the decontamination conditions (pH, temperature, ratio of solution volume to the mass of sorbent) shown that sorption of Fe-59, Cr-51 and Mn-54 on the silica gel at these conditions is rather high (Table 5).

TABLE 5. SORPTION OF RADIONUCLIDES ON SILICA GEL

pH of solution	Sorption of Cr-51 (%)	pH of solution	Sorption of Fe-59 (%)
3.5	8.3	1.5	14.4
3.8	10.6	1.8	20.0
4.0	19.4	2.0	34.3
4.5	34.2	2.4	67.3
4.9	61.5	2.8	83.8
5.2	73.7	3.0	90.9
6.0	97.5	3.2	96.4
6.7	99.0	3.5	98.6

The other method to increase decontamination efficiency for stainless steel with high content of chromium is to apply two stages decontamination treatment. It is known from the literature that the method of two stages' treatments should be applied for dissolving oxides' films with high content of chromium. On the first stage it is necessary to oxidise Cr (III) into more soluble Cr (IV) state, and on the second stage acidic solution of reductant or complexing agent is applied to dissolve the residual corrosive film.

Traditionally the widely used oxidation composition is alkaline solution of potassium permanganate (AP), consisting of potassium permanganate and sodium hydroxide. Potassium permanganate in basic solution oxidise chromium and transfer it to the solution. After this treatment the corrosion film became friable and that made application of the second stage of treatment more effective.

Before starting decontamination of real equipment different decontamination compositions were tested on the simulated samples of different construction materials. The results of some selected testing experiments are presented in Table 6.

It can be seen from the table that application of acidic solution of potassium permanganate is more effective for decontamination of stainless steel than application of basic solution of the same oxidation agent. It can be explained by the following considerations. Basic oxidation solution provides stainless steel the potential necessary for oxidation of Cr (III) to CrO_4^{2-}, which is soluble in the basic solution, and oxidation of Fe_3O_4 to Fe_2O_3 and FeOOH. Leaching of chromium and oxidation of Fe (II) increases concentration of defects and increases free energy of crystallite lattice of oxides, which work in favour of dissolution and destroying of oxides layer at the next step of decontamination. Chemical analysis of the first and the second decontamination solution has shown that the main part of chromium was transferred into the first solution, and other components of corrosion products – into the second solution (Table 7).

TABLE 6. DECONTAMINATION OF SIMULATED SAMPLES.
TREATMENT TIME 2 HOURS, T = 85 °C

Decontamination composition	Decontamination coefficient		
	Cr-51	Mn-54	Fe-59
1) 0.6% NaOH + 0.5% $KMnO_4$ 2) 2% $H_2C_2O_4$	150±50	300±70	100±40
1) 3% NaOH + 0.3% $KMnO_4$ 2) 1% $H_2C_2O_4$	290±40	200±30	200±30
1) 0.6% NaOH + 0.1% $KMnO_4$ 2) 0.2% $H_2C_2O_4$	60±15	50±15	40±10
1) 0.6% HNO_3 + 0.1% $KMnO_4$ 2) 0.25% $H_2C_2O_4$	500±100	300±80	300±40
1) 3% HNO_3 + 0.3% $KMnO_4$ 2) 1% $H_2C_2O_4$	890±40	770±40	800±40
1) 6% HNO_3 + 0.5% $KMnO_4$ 2) 2% $H_2C_2O_4$	5000±1000	5000±1000	4000±1000

TABLE 7. DISTRIBUTION OF RADIONUCLIDES (%) BETWEEN OXIDISING AND REDUCING DECONTAMINATION SOLUTIONS.
TREATMENT TIME 2 HOURS, T = 85 °C

Decontamination solution	Cr-51	Fe-59	Co-60	Mn-54
1) 3% NaOH + 0.3% $KMnO_4$	75	1	1	3
2) 1% $H_2C_2O_4$	25	99	99	97
1) 0.6% NaOH + 0.5% $KMnO_4$	80	2	1	4
2) 2% $H_2C_2O_4$	20	98	99	96

Further oxidation of the corrosion products during application of the decontamination solutions containing oxidants is going on the surface layer between metal and solution and very much depends on diffusion rate of metal cations to the surface.

The higher imperfection of crystallite lattice, the faster are the diffusion processes of metal's cations to the outer border between metal and solution, the faster are the oxidation processes. However, if the initial oxides layer on the surface of metal is hard, nonelectroconductive and non-porous, application of basic oxidation solution is not effective mainly because of slow diffusion and associated oxidation processes on the surface of the oxide's film. In this case application of acidic solution of oxidizing agent is more effective (Table 6). It can be seen from the Table 6 that decontamination coefficient in the case of application acidic solution of potassium permanganate on the first stage of treatment is much higher than in the case of basic solution of permanganate. So, in spite of the fact that acidic oxidation conditions are less appropriate for oxidation of Cr (III) , more favorable conditions for oxidation and dissolution of Fe_3O_4 leading to the increasing of total decontamination effectiveness. Oxidation of metal in acidic solution is performed at about the same level as in the basic solution, but simultaneously dissolution of Fe in base metal is taken place, which lead to the break off of corrosion products film and increase of the decontamination effect.

For etching of stainless steels and deleting hard corrosive films during decontamination sometimes the solutions containing fluoride ions could be recommended since the hydrofluoric acid at presence of other acids can work as a catalyst for dissolution of chromium and ferrous oxides. Different compositions contain fluoride ions were tested for decontamination of simulated samples of stainless steel X18H10T. The results obtained are presented in Table 8.

TABLE 8. DECONTAMINATION WITH COMPOSITIONS CONTAINING HF. DECONTAMINATION TIME 60 min, T = 22°C

Decontamination composition	Decontamination coefficient		
	Cr-51	Mn-54	Fe-59
40% HNO_3 + 5% HF	290±110	490±180	370±70
5% HNO_3 + 5% HF + 0.5% Na-hexametaphosphate	180±60	260±90	200±80
14% HNO_3 + 6% HF + 1% Na-hexametaphosphate	3500±500	4000±600	3500±500
20% HNO_3 + 6% HF + 2% Na-hexametaphosphate	4300±600	4900±800	4500±700

* Na-hexametaphosphate – ($Na_6P_6O_{18}$), or $(NaPO_3)_n \cdot H_2O$

It can be seen from the table that effectiveness of decontamination of stainless steel at presence of HF is quite high, especially at presence of complexing agents, in particular sodium salt of hexametaphosphoric acid – sodium hexametaphosphate. The latest forms soluble complexes with metal ions and prevents formation of secondary sediments on the treating surface. The optimal composition for decontamination can be recommended as the following:

- HNO_3 - 15%,
- HF - 5%,
- Na-hexametaphosphate - 1%.

Crumbly sediments and corrosion products on the surface of the equipment worked at low temperature and pressure can be deleted using single step treatment with diluted solutions of oxalic or citric acids, or basic solution of 0.4% 1-hydroxyethilidendiphosphone acid OEDPA (Table 9).

TABLE 9. DECONTAMINATION OF EQUIPMENT WORKED AT LOW PRESSURE (0.6-0.8 Mpa) AND TEMPERATURE (40-50°C).

Type of steel	Decontamination composition	Conditions of decontamination	Decontamination coefficient
08X18H10T	2% $H_2C_2O_4$	40°C, 1 hour	150±40
08X18H10T	2% $H_2C_2O_4$ + 0.5% citric acid	40°C, 30 min	180±40
12X18H10T	0.5% citric acid	40°C, 1 hour	45±15
08X18H10T	0.2% OEDPA + 2% NaOH	40°C, 1 hour	170±30

Decontamination of surfaces covered with solid dense oxides film requires application of more strong decontamination compositions and more complicated decontamination procedures. In this case application of two stages decontamination procedure and use of more strong and aggressive reagents are required to achieve effective decontamination. The results of application of some decontamination compositions for decontamination of dismantled NPP's equipment are presented in Table 10. In some cases two stages treatment was not effective for sufficient decontamination. In these cases of the same two stages procedures was more effective than just increasing of the treatment time. However such procedure substantially increase the amount of liquid secondary waste and would be not recommended for wide application.

Very effective decontamination composition containing nitric and hydrofluoric acids at presence of Na-hexametaphosphate was not used for full-scale decontamination of equipment so fare mainly because of aggressive nature of hydrofluoric acid, which create a lot of problems during processing of decontamination liquid waste. However just recently the method was found to solve this problem. The idea of the approach was to find a way to bind fluoride anions in non-aggressive durable compound and utilize this approach for treatment of spent decontamination solutions.

TABLE 10. DECONTAMINATION OF EQUIPMENT WORKED AT HIGH TEMPERATURE (400-450°C) AND PRESSURE (4.0-4.5 Mpa)

Type of steel	Decontamination composition	Conditions of decontamination	Decontamination coefficient
13X11H2B2MO	1) 5% HNO_3 + + 0.3% $KMnO_4$ 2) 2% $H_2C_2O_4$	50°C, 60 min	background
08X18H10T	1) 5% HNO_3 + + 0.3% $KMnO_4$ 2) 2% $H_2C_2O_4$	35°C, 50 min	150 ÷ 180
08X18H10T	1) 5% KOH + + 0.3% $KMnO_4$ 2) 2% $H_2C_2O_4$	60°C, 60 min	50 ÷ 80
20X23H18	1) 1.5% HNO_3 + + 0.3% $KMnO_4$ 2) 1% $H_2C_2O_4$	50°C, 120 min	120 ÷ 170
13X11H2B2MO	1) 5% KOH + + 0.3% $KMnO_4$ 2) 2% $H_2C_2O_4$	50°C, 60 min	150 ÷ 210

After finishing the experimental part of work the decontamination of high and low pressure turbines and loading-unloading installations had been performed. Such details of turbines as diaphragms, mounting, back walls, diffusors, nozzle apparatus, bearings, clip rings were decontaminated. Apart from the turbines decontamination of different pipelines, valves, controllers has been performed.

The main construction materials used in above mentioned details were chromium-nickel austenitic steels with high content of nickel, chromium steels and chromium-nickel steels with low content of nickel (Table 2).

Maintenance parameters of equipment were: temperature in range 50-450°C, pressure 0.8-4.4 atm.

Decontamination of the installations was performed by bath method. Mechanical action of brushes was used in some cases. Determing factor in selection of decontamination solution was the work temperature of installation, because chemical and phase composition of corrosion product deposits on the surfaces to be decontaminated depends namely on temperature.

Decontamination of equipment functioning at the temperature below 100°C

Taking into consideration interaction of N_2O_4/NO_2 with the surfaces of construction materials in low temperature regimes, employment of solutions containing organic acids, complex salts, Red-Ox components was reasonable. Organic acids possess high ability to create complexes with radionuclides, and they don't cause corrosion cracking of austenitic steels. Strong soluble complexes of organic acids with radionuclides prevent from forming the secondary deposits. The decontamination was carried out at the temperature about 25°C, during 1 hour.

The data obtained are presented in table 11.

TABLE 11. DECONTAMINATION OF INSTALLATION FUNCTIONING AT TEMPERATURE BELOW 100°C

Decontamination solution	DF
1,5% EDTA	20±5
0,5% $CH_3C(OH)(PO_3H_2)_2$ (HEDPA)	40±10
1% $H_2C_2O_4$	40±8
0,5% $H_2C_2O_4$ + 0,5% $(NaPO_3)_6$	80±30
0,5% HEDPA + 2,5% KOH (pH 11)	400±80
0,5% HEDPA + 2,5% KOH + 0,3% H_2O_2	550±70
0,5% HEDPA + 2,5% KOH + 0,3% H_2O_2 + N_2O_4 ($V_{N_2O_4} : V_{decont.sol} = 1:100$)	1000±200

Analysis of the data presented in table shows that decontamination ability of oxalic and hydroxyethilidendiphosphonic (HEDPA) and ethylendiaminotetraacetic (EDTA) acids at room temperature was not sufficient.

The alkaline decontaminating solutions containing HEDPA and hydrogen peroxide showed a good decontaminating ability because H_2O_2 displayed oxidising properties in alkaline media. However, H_2O_2 is not stable in solutions in presence of Fe(II) and Fe(III) ions. It's explained by the forming of intermediate compounds with catalyst, and namely that ions act as catalysts. At the same time HEDPA stabilises H_2O_2 due to the fact of containing of aliphatic oxygroup in this acid, the latter has a good ability for the forming of strong soluble complexes with metal-ions in a wide range of pH value.

Experiments of maintenance of mobile power plant with coolant N_2O_4 showed that complete removing of coolant was very difficult operation. In practice, the products of interaction of coolant with water such as nitric and nitrous acids were presented in decontamination solutions during washing. Decontamination ability of the solutions did not get worse. Addition of some quantity of coolant to the decontaminating solution elevated the value of DF (Table 11) because of high oxidising properties of nitrous acid and its salts.

Taking into consideration high decontamination effectiveness of the compositions for stainless steels the possibility of its use for loading-unloading equipment decontamination was tested.

Investigations of corrosion resistance of construction materials in decontaminating solution containing 2,5% KOH + 0,5%HEDPA + 0,3%H_2O_2 + N_2O_4 ($V_{N_2O_4}$ / V_{sol} = 1:100) included tests on general, chink and contact corrosion of different stainless steels.

Influence of decontamination medium on corrosion of steels was investigated by consecutive treatment of samples by the decontamination solution during 1 hour at 25°C, and then by washing of samples by water during 15 min. The cycle of treatment was repeated 12 times. Besides, resistance to general corrosion was investigated in solution with increased concentration of H_2O_2 up to 3% with unchanged concentration of other components.

Analysis of the tests showed that the loss of samples mass for all sorts of stainless steels during 12 cycles of treatment was insignificant. It's value was $2{,}9 \cdot 10^{-5}$ - $1{,}7 \cdot 10^{-4}$ g/cm^2 and it corresponded to corrosion spead value of $0{,}24 \cdot 10^{-5}$ - $0{,}14\ 10^{-4}$ g/cm$^2 \cdot$ h. The least mass losses were observed for steel type 10X13, the largest ones - for steel type 01X18H10T. The state of the samples surface remained unchanged.

Increasing of H_2O_2 concentration in decontamination solution elevated considerably corrosion loss of samples masse up to $7{,}1 \cdot 10^{-2}$ g/cm^2 (steel type 95X18). Only such steel types as 35X15H3Б and 14X17H2 were resistant in decontamination solution with increased concentration of H_2O_2.

Changes of samples surface state were more essential in solution with increased concentration of H_2O_2 too.

Investigations of chink corrosion showed that local corrosion of samples in apertures 0,2 and 0,1 mm was not observed. Changing of samples surface state took place in aperture clearance 0,1mm in size only for several types of steel.

Tests on contact corrosion showed that the influence of contact of tested types of steels in experimental conditions was not observed.

The results of metallographic analysis revealed the absence of general, contact, aperture and intercrystallite corrosion.

Selection of decontaminating solutions for the equipment functioning at the temperature of 200°C

On functioning of installation in temperature range from 100 to 200°C concentration of Fe in the corrosion deposits was 20%. As it was determined earlier oxalic acid was the most effective and universal reagent for the ferric oxides. Other decontaminating solutions were used for cleaning of equipment too. The results of decontamination are presented in table 12.

TABLE 12. DECONTAMINATION OF EQUIPMENT FUNCTIONING AT TEMPERATURE 100-200°C

Type of steel	Decontamination solution	Conditions	DF
13X11H2B2MФ	2% $H_2C_2O_4$ +1%H_3 Cit	40°C, 60 min	150±20
13X11H2B2MФ 14X17H2	2% $H_2C_2O_4$ +0,5%H_3Cit	20°C, 40 min	120±20
12X18H10T	2% $H_2C_2O_4$+ +0,5%H_3Cit + +0,1% HEDPA	60°C, 40 min	180±30
20X13	2%$(NH_4)_2S_2O_8$ + 1% H_2SO_4	25°C, 20 min	40±10
08X18H10T X18H10T	5%$(NH_4)_2S_2O_8$ + 2% H_2SO_4+0,1%H_3PO_4	40°C, 30 min	120±30
X18H10T	5%$(NH_4)_2S_2O_8$ + 2% H_2SO_4+ 0,1% H_3PO_4	70°C, 60 min	250±40
08X18H10T 12X18H10T 20X23H18	1% KOH + 0,3%HEDPA + 0,3% H_2O_2	40°C, 30 min	220±40

Decontamination of equipment functioning at temperature 300 - 500°C

At the temperature range from 300 to 500°C under influence of dissociating coolant N_2O_4/NO_2 steel surface was covered by oxide films presented by Fe_2O_3; Cr_2O_3; NiO. These oxides were to be removed by red-ox solutions. The results of decontamination of high pressure turbine are presented in Table 13.

Corrosion of steels after decontamination by these solutions did not exceed the standard value.

The residual activities of turbine elements after decontamination were 2-10 Bq/cm^2.

TABLE 13. DECONTAMINATION OF EQUIPMENT WORKED AT TEMPERATURE 300-500°C AND PRESSURE 4.0-4.5 MPa

Type of steel	Decontamination solutions	Conditions	DF
13X11H2B2MΦ	1) 5%KOH+ 0,3%$KMnO_4$ 2) 2% $H_2C_2O_4$+ 0,3% H_2O_2	60°C, 40 min	220±30
X18H10T	2%$(NH_4)_2S_2O_8$ + 1% H_2SO_4	40°C, 30 min	200±30
13X11H2B2MΦ 20X23H18	1) 1,5% HNO_3 + 0,3% $KMnO_4$ 2) 1% $H_2C_2O_4$	60°C, 40 min	120±30
20X23H18 14X17H2	1) 5%KOH + 0,3% $KMnO_4$ 2) 2% $H_2C_2O_4$	90°C, 30 min	back-ground
20X23H18	1) 3% HNO_3 + 0,1% $KMnO_4$ 2)1% $H_2C_2O_4$	50°C, 60 min	240±40
08X18H10T	1) 5% HNO_3 + 0,5% $KMnO_4$ 2) 2% $H_2C_2O_4$	50°C, 60 min	530±60
08X18H10T	1) 7% HNO_3 + 0,5% $KMnO_4$ 2) 2% $H_2C_2O_4$	90°C, 40 min	back-ground

At present the work on decontamination of technological equipment and rooms of trial building, liquid radioactive waste management is carried out.

SUMMARY

The purpose of the work was to check applicability of the existing and new compositions for decontamination and their adjustment to the specific conditions dealing with operation of the research reactor with N_2O_4/NO_2 cooling system.

Determining factor in selection of decontamination solution was the work temperature of installation, because chemical and phase composition of corrosion product deposits on the surfaces to be decontaminated depends namely on temperature.

Experiments have shown that the simple acid compositions are not effective for decontamination of stainless steels exposed in N_2O_4/NO_2 at high temperature and pressure. To improve effectiveness of decontamination several approaches have been tested.

Application of acidic solution of potassium permanganate is more effective for decontamination of stainless steel than application of basic solution of the same oxidation agent.

Decontamination ability of solutions containing 1-hydroxyethylidendiphosphonic acid, hydrogen peroxide and ammonium persulphate was high.

Investigations of corrosion resistance of construction materials in tested decontamination solutions showed the absence of general, contact, aperture and intercrystallite corrosion.

COMPARISON OF THOROUGH DECONTAMINATION TECHNIQUES ON DISMANTLED PIECES OF A PWR REACTOR

XA9847482

M. KLEIN, A. RAHIER, R. MANDOKI, M. PONNET
SCK-CEN Belgian Nuclear Research Centre
Mol, Belgium

Abstract

The decontamination experience gained during the BR3 dismantling project is developed. This started with the full system decontamination of the primary loop and was followed by R&D on thorough decontamination projects. First, a wet abrasive installation has been installed and is now in operation for the thorough cleaning of metallic pieces of simple geometry. Afterwards, the chemical cerium process has been developed. The results of the regeneration with ozone and with electrochemistry are presented in detail. The ozone regeneration process has been selected for the industrial installation of which the construction is foreseen in 1998.

1. INTRODUCTION

The dismantling of the BR3 will lead to the generation of a great amount of contaminated metallic waste. For the BR3, this mass is estimated at about 600 t of C-steel and of stainless steel mainly. It is of great economical importance to reduce the amount of contaminated material which must be treated as radioactive waste; therefore very efficient decontamination techniques have to be used so that the decontaminated material can be evacuated as non radioactive waste or at least recycled as very low radioactive material.

A R&D and demonstration project on thorough decontamination processes for metallic pieces was then launched. This project deals not only with the contaminated pieces which will arise from the dismantling of the BR3 reactor, but is also examining other materials such as Al and Pb and other contamination sources.

2. OVERVIEW OF THE BR3 DISMANTLING ACTIVITIES

The BR3 PWR reactor, shutdown in 1987, has been selected by the EC as one of the four pilot dismantling projects in the framework of its dismantling R&D programme on decommissioning of nuclear installations.

The decommissioning activities started in 1989 and the main activities performed till now are:

- the full system decontamination of the primary circuit in 1991 leading to a global dose rate reduction by a factor of 10;
- the segmentation of high active internals: the thermal shield, the Vulcain internals, the Westinghouse internals using underwater remote techniques such as plasma cutting, electro erosion cutting, milling cutter and band saw;
- the evacuation and conditioning of high active waste by cement embedding by the BELGOPROCESS company;

- the preparations for the segmentation of the reactor pressure vessel including the selection of the dismantling strategy (comparison between underwater and in air dismantling; comparison between in-situ dismantling in the reactor cavity and one piece removal followed by dismantling in the refueling pool), the radiochemical characterisation of the vessel and the study of the adaptations of the tools;
- the dismantling of various contaminated auxiliary circuits and the sorting out of the dismantled pieces in function of the selected evacuation route (radioactive waste, melting for recycling or for free release, decontamination);
- the decontamination by several techniques (washing, wet abrasive blasting, dry polishing) of the dismantled pieces and their evacuation as non radioactive material to a classical recycling foundry. Till now about 34 tons of metals have been free released.
- the recycling of slightly contaminated or activated metallic pieces by melting in a "nuclear" foundry and fabrication of recycled material for the nuclear industry. Till now about 8.2 t have been melted in the SEG foundry of Westinghouse in the USA and the evacuation of 28 t is under preparation. It is foreseen to further use this route at a capacity of about 20 to 40 t/year. This route is also used for materials arising from other dismantling activities at SCK•CEN e.g. for the evacuation of aluminium heat exchangers.
- the characterisation by core drilling and the modellization of the activation of the heavy concrete of the bioshield around the reactor pressure vessel;
- studies and tests on decontamination and demolition techniques for activated and contaminated concrete (scabbling, hydraulic jack hammer, explosives, diamond sawing);
- the decontamination by scabbling techniques of about 250 t of contaminated anti-missile heavy concrete slabs from which 74% could be free released and recycled in the construction industry. The rest is either slightly activated (17%) or requires additional measurements before the free release (9%);
- the removal, from the primary and auxiliary circuits situated in the plant container, of contaminated isolation material containing asbestos. This work is still in progress and is planned to be finished in February 1998. Till now about 200 drums of this mixed waste have been produced. They will be conditioned by supercompaction followed by cement embedding at Belgoprocess;
- R&D programme on thorough decontamination techniques for contaminated metals.

Detailed information on the decommissioning and decontamination activities can be found in [1] [2] [3] [4].

3. OVERVIEW OF THE EVACUATION ROUTES FOR RADIOACTIVE MATERIALS

The high and medium active radioactive wastes are conditioned and temporarily stored in the installations of Belgoprocess which is situated close to the research centre. There are no final storage available for the moment in Belgium. Studies are performed by ONDRAF/NIRAS for the shallow land burial for the low radioactive wastes and for disposal in a clay formation for the high level and long lived radioactive wastes.

The dismantling of contaminated loops and equipment, as well as some buildings and walls, involves the problem of the management of large amounts of low level waste (LLW) or even V(Very)LLW. Considering the cost of radioactive waste storage and disposal, and its

escalation, we try to recycle in the nuclear industry or to decontaminate as much materials as possible to reach either the recycling limits or the free release levels. As such, the amount of materials to be considered as radioactive waste can be decreased drastically.
The amount and types of materials and contamination levels being quite large, and the authorities requesting a good traceability of the material history and handling, a complete computerised material flow management system has been set up [5] . This allows to know at each time the current situation of the waste/material stream, and also to follow each piece (or set of similar pieces, the system being based on batches) throughout the different routes, from the dismantling on site to the evacuation as non-radioactive material or as radioactive waste.
This system is also linked with the plant inventory and allows to define the quantities and costs associated with the handling of the materials.

The main evacuation routes used up to now are:

- unconditional release for disposal as industrial waste,
- unconditional release for recycling e.g. scrap metals, concrete rubble...
- recycling after melting e.g. C-Steel, SS Steel, Al for fabrication of shielding blocks, waste containers...
- radioactive waste conditioned by Belgoprocess by incineration, super-compaction, cement embedding in the CILVA installation.

SCK•CEN has set up a free release procedure in agreement with the Control Organism (AVN) and the Competent Authority (Ministery of Health). This procedure allows to free release radioactive materials following two different ways. The first one is based on a 100% surface measurement respecting the surface contamination limits of 0.4 Bq/cm^2 for β, γ nuclides and 10 times lower for α emitting nuclides. Two successive measurements are required; the second one must be done after a 3 months delay storage if the piece has been decontaminated.
The second one is based on the measurement of the mass contamination (e.g. for concrete rubble) and the comparison with the guidance values from the IAEA and EU studies. For the mass contamination, the free release is a case by case decision depending on the final destination of the waste. The authorisation for free release is given by the Health Physics of the site after consultation of the Control Organism.

4. PREDISMANTLING FULL SYSTEM DECONTAMINATION OF THE PRIMARY LOOP OF THE BR3 REACTOR

The Full System Decontamination performed by the CORD process in collaboration with Siemens KWU led to the removal of about 2 TBq of ^{60}Co and 2.3 GBq of alpha activity. The CORD process comprises 3 successive steps : an oxidation step with permanganic acid, a decontamination step with oxalic acid and a cleaning step on ion-exchange resins. For the BR3 system, 3 successive decontamination cycles at an operating temperature of 80 to 100°C were performed; the operation itself lasted nine days of continuous operation. The only solid waste generated were exhausted anionic and cationic resins; a total quantity of 1.37 m^3 was used. The resins were conditioned by concrete embedding in 400 l drums giving rise to the production of a final waste volume of 7.6 m^3.

This resulted in a mean decrease by a factor 10 of the dose rate on the contaminated equipments of the primary circuit and of the purification circuits. The residual specific activity lies now between 1000 and 10,000 Bq/cm^2. This corresponds to an ambient dose rate in the vicinity of these equipments of about 0.06 to 0.1 mSv/h. This dose rate will allow further hands on dismantling with a reasonable dose uptake by the operators.

The chemical decontamination appears to be very cost effective in man-Sv exposure reduction. Indeed, only 0.158 man-Sv was attributed to the operation. It is estimated that the dose rate reduction will lead to a dose savings of 4.25 man-Sv for the future dismantling operations. It must be noted that the decontamination operation had two unexpected effects. First, a pollution of the reactor pool occurred during the unloading of the reactor internals resulting in a high turbidity and low visibility in the pool; this pollution was due to the presence of insoluble ferrous oxalate and loose crud still present on the internals. Secondly, the internals of the reactor were remarkably clean. This greatly facilitated the subsequent dismantling operations and even allowed to evacuate 35% of the reactor internals (i.e. 5 tons) as Low Active Waste (LAW).

5. OBJECTIVES OF THE THOROUGH DECONTAMINATION PROGRAMME

The main objective is to minimize the quantity of radioactive waste produced by the dismantling activities of the BR3 reactor.

The dismantling will produce a variety of metallic wastes:

- C-steel painted structural equipments slightly contaminated (1 to 20 Bq/cm^2 typically) by deposition of airborne contamination, liquid spilling or by prolonged contact with contaminated liquids (typically pool water).
- C-steel equipment slightly (10 to 200 Bq/cm^2) or heavily contaminated (> 1000 Bq/cm^2): reservoirs, heat exchangers and piping.
- SS steel equipment with crud deposit (1000 to 50,000 Bq/cm^2) : reservoirs, heat exchangers, primary piping, auxiliary circuits...
- C-steel equipment with SS cladding or with SS parts: typically the pressurizer, the steam generator, heat exchangers.
- Aluminium pieces and lead shielding.

To treat these various types of contaminated materials, it is necessary to have a variety of decontamination processes such as:

- Physical methods: abrasives wet or dry;
- Electrochemical methods: anodic electropolishing;
- Chemical methods: agressive processes with regeneration of reagents.

6. PHYSICAL DECONTAMINATION PROCESS: THE WET ABRASIVE PROCESS

CEN•SCK has selected a Wet Abrasive Cleaning method for the decontamination of pieces of simple geometry externally contaminated mainly for structural pieces of painted carbon steel.
A commercial installation from the company Vapormatt has been purchased and installed in a stainless steel walk-in ventilated booth.

The main characteristics of this installation called ZOE (Zandstraal Ontsmetting Eenheid) are:

- dimensions of the ventilated walk-in booth: 3x3x3 m^3;
- possibility to work inside with a ventilated suit or from outside with the gloves;

- an abrasive gun with mixing of compressed air and liquid charged with abrasives and circulated by a vortex pump;
- a rinsing gun with filtered water and compressed air;
- a rinsing gun with fresh water;
- recycling of the abrasives with the vortex pump;
- separation of the sludge from the abrasives by sedimentation;
- recycling of the rinsing water by filtration on cartridge filters;
- ventilation of the booth at a flow rate of 3000 m^3/h and filtration with an electrostatic filter and two HEPA's in parallel by two fans operating in parallel.

Figures 1 and 2 show the ZOE installation.

A first exploitation campaign was made between April and October 1996. During this campaign, 10 t of metallic pieces were treated; 6.3 t were slightly activated and could not be free reelased, the rest 3.7 t was free released unconditionnally. The corresponding total surface treated was 62 m^2.

During this campaign, several abrasives were tested (alumina, zirconium oxide and stainless steel grit). The alumina abrasive is not hard enough for the type of materials treated, the ceramic abrasive was only used during a short period and mainly stainless steel grit was used because of its hardness. However, the effective cleaning capacity (expressed in m^2 of surface treated per effective working hour) was rather low. It varied between 0.1 and 1.2 m^2/h with a mean value of about 0.41 to 0.49 m^2/h.

This capacity is too low and improvements were made to the installation. A new turbine was installed in the Vortex pump and the ceramic abrasive was used instead of stainless steel

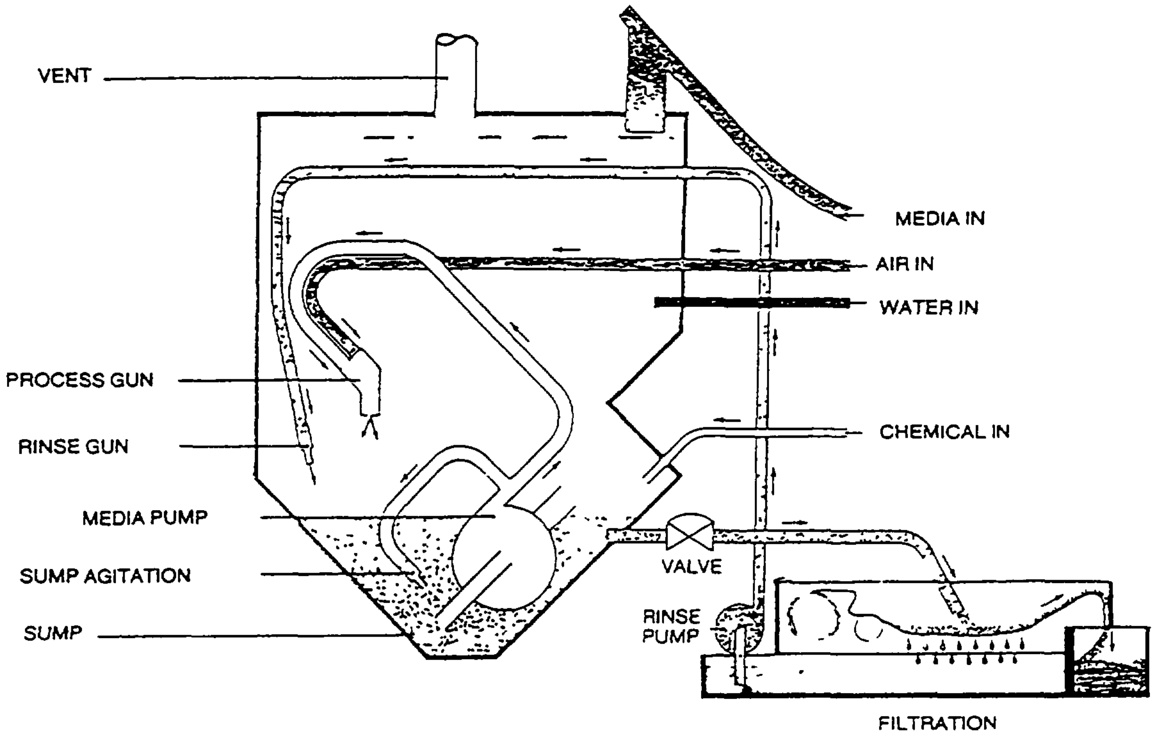


FIG 1 Wet abrasive decontamination unit

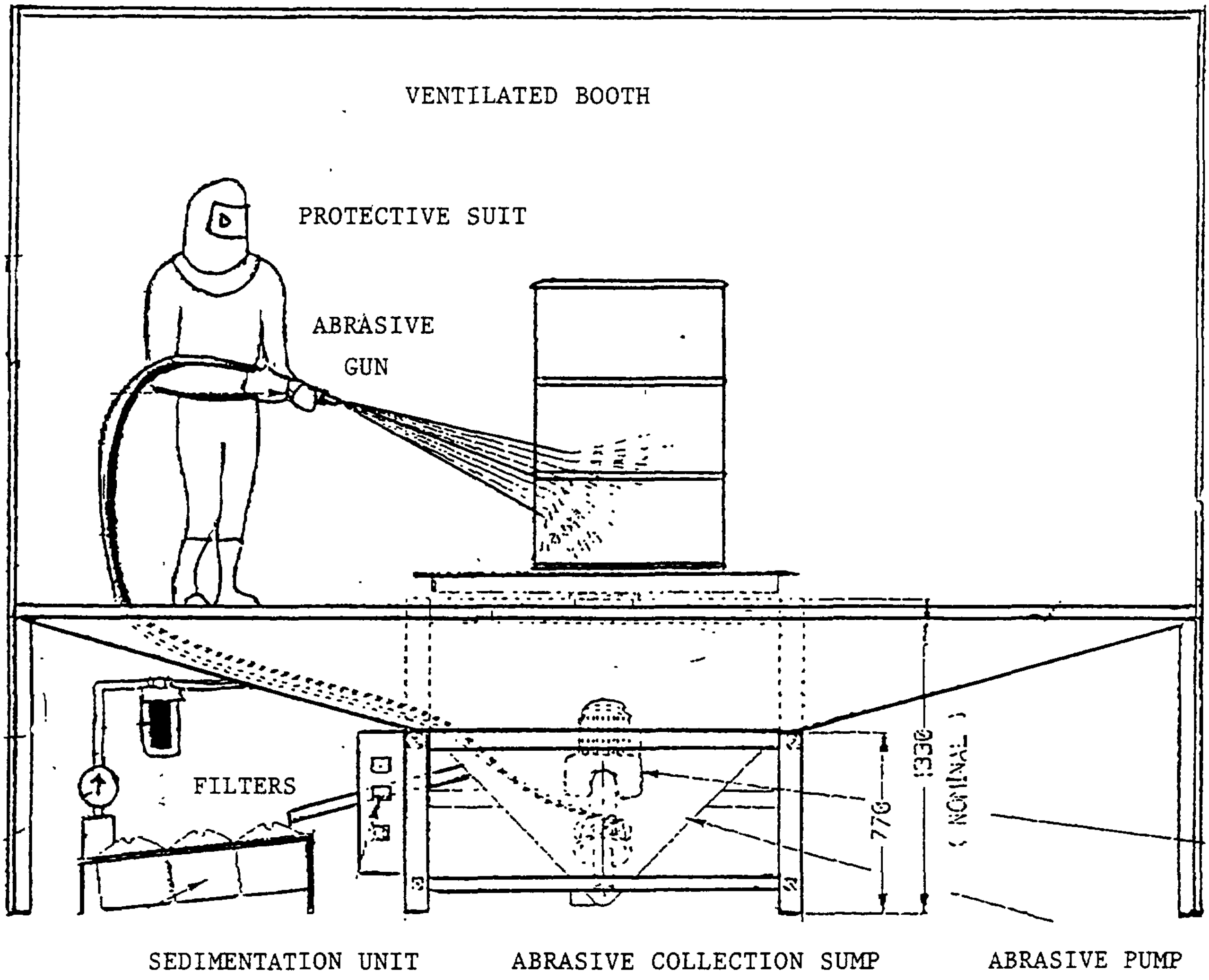


FIG.2. Wet abrasive decontamination unit in walk in booth.

because of its lower specific gravity. This allowed to increase the liquid flow rate of the vortex pump and to increase the concentration of abrasives in suspension so that the abrasive flow in the process gun was significantly increased.

During the second exploitation campaign performed between march and may 1997, a total mass of 2.15 t was treated (corresponding to a total surface treated of 55 m^2). The effective cleaning capacity varied between 0.3 and 3.9 m^2/h depending mainly on the nature of the surface treated. The mean value is now about 1.3 m^2/h which represents an increase by a factor 2.5 vs the first exploitation campaign. Only 10% of the treated mass could not be free released; this was due to the complex geometry of these pieces.

During this period, a mass balance was made to determine the consumption of the raw materials and the production of the secondary wastes. This mass balance is given in Table I.

Table I : Mass balance of the ZOE installation - Campaign nr 2 - March to May 1997

	Raw materials		**Secondary wastes**	
Abrasives	1.37	kg/m^2	0.57	dm^3/m^2
Filter cartridges	0.07	units/ m^2	0.28	dm^3/m^2
Absolute filters	0.003	units/ m^2	0.003	$units/m^2$
Protective cloths	1.25	units/ m^2	4.15	dm^3/m^2
Solid waste (paper, gloves..)			0.7	kg/m^2
Liquid waste (water)			0.05	m^3/m^2

This table shows:

- a low abrasive consumption thanks to the recycling of the abrasive in a closed loop;
- a low water consumption thanks to the water recycling by filtration;
- a high amount of expensive protective cloths used with a resulting high volume of secondary waste produced.

Since then, an additional quantity of about 1.7 t was treated with about 9.4 % not free released and sent to the melting route for recycling.

As conclusion, it can be stated that:

- the wet abrasive technique is efficient for pieces of simple geometry with all the surfaces easily accessible;
- the use of expensive protective cloths and the associated waste have a strong impact on the treatment cost;
- the work organisation (in and output of the pieces, manipulation, measurements...) could still be improved to further reduce the overall treatment cost.

This installation allows us now to free release contaminated metallic materials at an overall cost lower than the evacuation as radioactive waste. Some additional improvements will be realised in the near future to further reduce this cost. More attention will also be paid to the selection of the pieces to treat (no complex geometry, minimum thickness, avoid the presence of contaminated welds...).

7. CHEMICAL DECONTAMINATION METHODS

These methods are mainly developed for the piping and equipments in stainless steel which have been in contact with primary water at reactor operating conditions.

7.1. Characterisation of the contamination

The primary circuit and its associated circuits are internally contaminated by corrosion-erosion products, forming the so-called CRUD layer, containing mainly Co^{60} as contaminant.

Most of the pieces are in Stainless Steel 304. For the parts which have seen the Full System Decontamination with the CORD process, the residual contamination lies between 10^3 and 5.10^3 Bq/cm^2 gamma emitters; for the parts which are still covered with the original crud deposit, the contamination lies between 10^4 and 5.10^4 Bq/cm^2. The gamma spectrometry analysis of the crud shows that, at the reference date of 1995/1/1 i.e. about 8 years after the reactor shutdown, the dominating nuclide is **Co-60**. **Mn^{54}** is still present at about 0.14 % and **Cs^{137}** as contaminant at about 0.3 % to 0.6 %.

7.2. Decontamination tests at laboratory scale on contaminated samples

The first step in the research programme was to compare, at laboratory scale on active representative samples, the effectiveness of two types of chemical decontamination processes. The first one was a classical two-step oxidation-reduction process (CORD or CONAP process), which dissolved the oxide layer (the so-called CRUD) completely without attacking the base metal. The second type was one-step chemical processes, which remove the contamination by attacking the base metal as well. Two such processes have been tested, the first one based on a mixture of nitric and hydrofluoric acids at low concentration and the second one based on Ce^{4+}, a strong oxidant dissolving both the oxide layer and the base metal. All these processes could achieve decontamination factors higher than 10^4 leading to very low residual activities of the treated pieces allowing their possible evacuation as non radioactive waste. Residual activities lower than 0.3 Bq/g could be achieved on slightly contaminated pieces (1000 to 2000 Bq/cm2 of initial activity) and on highly contaminated pieces (about 6.10^4 Bq/cm2).

7.3. Decontamination tests at pilot scale

One process of each type, respectively the CORD process and the Ce^{4+} process were further selected on the basis of their operational advantages and tested at a semi-pilot scale in the so-called DECOLOOP allowing tests with pipe lengths up to 60 cm length.

The results obtained in the DECOLOOP have shown that both type of processes can achieve the required very low residual contamination level (the objective is to reach a Co^{60} activity lower than 0.3 Bg/g) and that the use of Ultrasonic power enhances the decontamination effectiveness.

The CORD and the Cerium processes were also successively used for the thorough decontamination of a heat exchanger, the so-called Regenerative Heat Exchanger (RHX).

The Cerium process shows some interesting features; it can be operated at a low temperature of about 60°C to 80°C, the Ce^{4+} can be regenerated with ozone or electrochemically, and the combination of attack of the oxide layer and of the base metal ensures that very low residual activity levels can be achieved.

The Cerium process was selected for the thorough decontamination of the dismantled pieces.

7.4. Regeneration of the cerium solution with Ozone

The ozone can oxidize the Ce^{3+} into Ce^{4+}in the acidic decontamination solution:

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

The experiments were performed at laboratory scale using a small laboratory ozone generator with a capacity of 2.2 10^{-3} mole O_3/h. The contact between the decontamination solution was performed in a small washing column.

A series of experiments were performed with air and oxygen as carrier gas and at different temperatures. The regeneration efficiency, defined as the theoretical amount of ozone needed to regenerate the measured cerium 4+ output vs the ozone output of the generator, is much better when oxygen is used as carrier gas vs air. The regeneration efficiency increases also in function of the operating temperature. At an operating temperature of the decontamination of 70°C, a regeneration efficiency of about 70% was obtained.

Corrosion tests on inactive SS304 samples were also performed to determine the corrosion rate and the effect of the ozone regeneration. The results indicate the positive effect of the use of ozone on the corrosion rate; at 70°C, a corrosion rate of about 2µm/h was obtained.

The results of decontamination tests performed on samples covered with contaminated crud. show again the efficiency of the process and the possibility to reach very low residual contamination for an operation time of 2 to 5 hours removing maximum 10 µm.

A pilot scale unit in industrial glassware has further been used to confirm the laboratory results and enable extrapolation to an industrial scale unit.

The regeneration tests were performed using an installation comprising a glass reservoir of 80 l capacity and a washing column filled with packing materials as gas-liquid contactor. The liquid is recirculated continuously and the oxygen laden with ozone (ozone generator of 0.1 to 0.13 mol/h O_3) is injected at the bottom of the column and flows upwards.

The tests were performed using a Ce^{3+} solution. The solution was brought to the desired temperature and oxygen/ozone gas was injected. The Ce^{4+} concentration in the solution was measured in function of the regeneration time. The results of the regeneration test performed at 80°C are shown, as example, in Figure 3. From these data, the Ce^{4+} production rate and the regeneration efficiency could be determined. The results are given in the table II.

Table II : Regeneration efficiency at pilot scale with the washing column

Temperature	**Mean Ce 4⁺ Production**	**Ozone Efficiency**
°C	mol/h	%
20	0.10	40
50	0.12	40
50	0.16	60
60	0.13	55
80	0.18	70

In the pilot unit, some decontamination tests were performed with ozone regeneration so that the Ce^{4+} concentration could be maintained constant throughout the whole test. Inactive samples of SS304, SS316 as well as contaminated stainless steel samples from different origins were treated at 80°C during 3 to 5 hours.

These tests confirmed :

- a corrosion rate of about 2 to 3 µm/h for the inactive not attacked samples,
- a corrosion rate of about 2 to 4 µm/h for the contaminated and attacked stainless steel samples,
- even with highly contaminated samples e.g. samples originated from dismantling of hot cells and strongly contaminated in Cs^{137} and alpha contaminated or with samples covered with PWR crud, the removal of about 10 µm is generally sufficient to completely remove the contaminated layer and to reach the free release level.

7.5. Theoretical and Experimental Study of the Selective Oxidation of the Cerous Ion on a Pt-Ti Anode in Sulphuric Acid Solutions

Prior to design the plant at industrial scale, it is important to get a good understanding of the physicochemical and electrochemical phenomenons involved in the regeneration technique. Related to this, one of the key questions to consider when regenerating anodically Ce^{4+} from Ce^{3+} is the selectivity of this process with respect to the oxidation of water. The purpose of the present work is to derive and assess a model describing the selectivity at the anode. The model allows to quantify the effect of the most important process variables on the anodic selectivity, thereby facilitating the design at an industrial scale.
According to the thermodynamic data, the ceric ion should not exist in aqueous solution since its standard potential (1.46 V) is higher than the one related to the oxidation of water (1.23 V). However, the kinetic of the oxidation of water by the ceric ion is slow enough to stabilize the latter in the presence of sulphuric acid [8]. Also, when regenerating the ceric ion on a platinum anode, a non negligible part of the total current can be spent to oxidize water, thereby lowering the current selectivity. The theoretical model describes the competition between the oxidation of the cerous ion (equation 1) and the oxidation of water (equation 2).

$$Ce^{4+} + e^- \rightarrow Ce^{3+} \qquad [1]$$

$$O_2 + 4\,H^+ + 4\,e^- \rightarrow 2\,H_2O \qquad [2]$$

We made several assumptions to elaborate the model. For instance, it is known that the oxygen evolution reaction on platinum is irreversible [9]. Hence, a Buttler-Volmer equation reduced to its Tafel form is valid to describe the overvoltage associated to the oxidation of water (equation 3). In the case of cerium, we assume that the electrochemical charge transfer is fast enough to put the process under diffusion control. An adequate description of this regime requires a logarithmic relation between the anodic overvoltage and the normalized current density (equation 4)[9].

$$\eta_{H_2O} = \frac{RT}{(1-\alpha)zF}\ln i_2 - \frac{RT}{(1-\alpha)zF}\ln i_0 \qquad [3]$$

where :

η_{H2O} is the overvoltage associated to the oxidation of water on a platinum electrode,
i_2 represents the current density corresponding to the oxidation of water,
i_0 is the exchange current density corresponding to the oxidation of water,
z is the number of electrons involved in the rate determining step,
α is the transfer coefficient associated to the oxidation of water,
while R, T and F have their usual meanings.

$$\eta_{Ce} = -\frac{RT}{F}\ln(1-\frac{i_1}{i_d}) \qquad [4]$$

where :

η_{Ce} is the overvoltage associated to the oxidation of the cerous ion,
i_1 is the current density corresponding to the effective oxidation of the cerous ion,
and i_d is the limiting current imposed by diffusion control.

$$i_d = \chi (Ce^{3+})^{\upsilon_1}$$

$\chi = (FD)/\delta$ in steady state operation, with D being the diffusion coefficient of the cerous ion and δ representing the thickness of the diffusion layer.
ν_1 is supposed to be close to unity. However, we expect that most deterministic parameters will have apparent values as a result of the particular geometry of the electrolysis cell being used and of the effect of the hydrodynamic regime on the thickness of the diffusion layer. For this reason, we prefer to consider this exponent as being a priori unknown.

For both reactions, an expression of the total electrode potential E with respect to the hydrogen reference electrode can be written by cumulating the thermodynamic contribution (Nernst) and the corresponding overvoltage. Eliminating E from these expressions, and assuming that both the partial pressure of oxygen and the activity of the proton remain constant, we obtain a relation between i_1 and i_2
The mathematical development is given in detail in reference [14]

The selectivity is defined as the ratio of the current used for the cerium oxidation i_1 on the total current consumed i_{tot}.

$$\xi = \frac{i_1}{i_{tot}} \qquad [5]$$

We obtain finally,

$$\frac{\theta}{i_{tot}} \bullet \left[\frac{\chi\gamma}{\chi - \xi \bullet i_{tot}\left[\frac{1+\gamma}{C_t}\right]^{\upsilon_1}}\right]^{z(1-\alpha)} - 1 + \xi = 0 \qquad [6]$$

Note that we posed:

$$\theta = zFk_0 \bullet \exp\left[\frac{(1-\alpha)zF}{RT}\left(E_1^0 - E_2^0\right)\right] \qquad [7]$$

k_o is the electrochemical kinetic constant for the oxidation of water combined with adequate functions of the proton activity and the partial pressure of oxygen. This parameter depends on the absolute temperature according to the Arrhenius law;
E^o_1 and E^o_2 are the standard potentials associated to equations 1 and 2 respectively,
and γ is the ceric ion concentration divided by the cerous ion concentration (= $[Ce^{4+}]/[Ce^{3+}]$)
C_t is the total concentration of cerium in the solution

Note that this expression is implicit and that the selectivity (ξ) depends on the concentrations (γ), on the temperature (θ , χ) and on the particular mechanism involved in the electron transfer for the oxidation of water (θ , z and α). Assuming that two electrons are transferred during the rate determining step, and that the transfer coefficient of this step is 0.5, the implicit character of equation 6 disappears. Common algebraic manipulations lead to a simplified expression for the selectivity as given by equation 8. This expression will be fitted to the experimental result to get an estimation of each parameter.

$$\xi = \frac{\chi}{2i_{tot}}\left[Ce^{3+}\right]^{\upsilon_1} + \frac{1}{2} - \sqrt{\left(\frac{\chi}{2i_{tot}}\left[Ce^{3+}\right]^{\upsilon_1} + \frac{1}{2}\right)^2 - \frac{\chi}{i_{tot}^2}\left[i_{tot} - \gamma\theta\right]\left[Ce^{3+}\right]^{\upsilon_1}} \qquad [8]$$

Experimental

Figure 4 shows the details of the small mock-up cell that has been used to measure the anodic selectivity. Both the anolyte and the catholyte are circulated in closed loops under atmospheric pressure and controlled temperature.
Both electrodes were cut out of a platinum sheet. They had the same area (7 cm²). The current was brought to the electrodes through two stainless steel plates. A platinum wire was inserted into each cell compartment to allow the monitoring of the voltage difference between each electrode and the bulk. Nafion 350 was used as separator. The leaktightness of the whole system was ensured by means of Teflon sheets and rings pressed between each parts of the cell.

Several experiments have been carried out using different conditions as reported in table III.

Table III : Experimental range of process variables

Variable	**Range**
Total cerium concentration	from 24 to 87 mol/m³
Initial $[Ce^{4+}]/[Ce^{3+}]$ ratio (γ)	from 0 to 1
Total current density	from 100 to 200 A/m²
Temperature	50 and 80 °C
Total duration of experiment	from 300 to 470 min

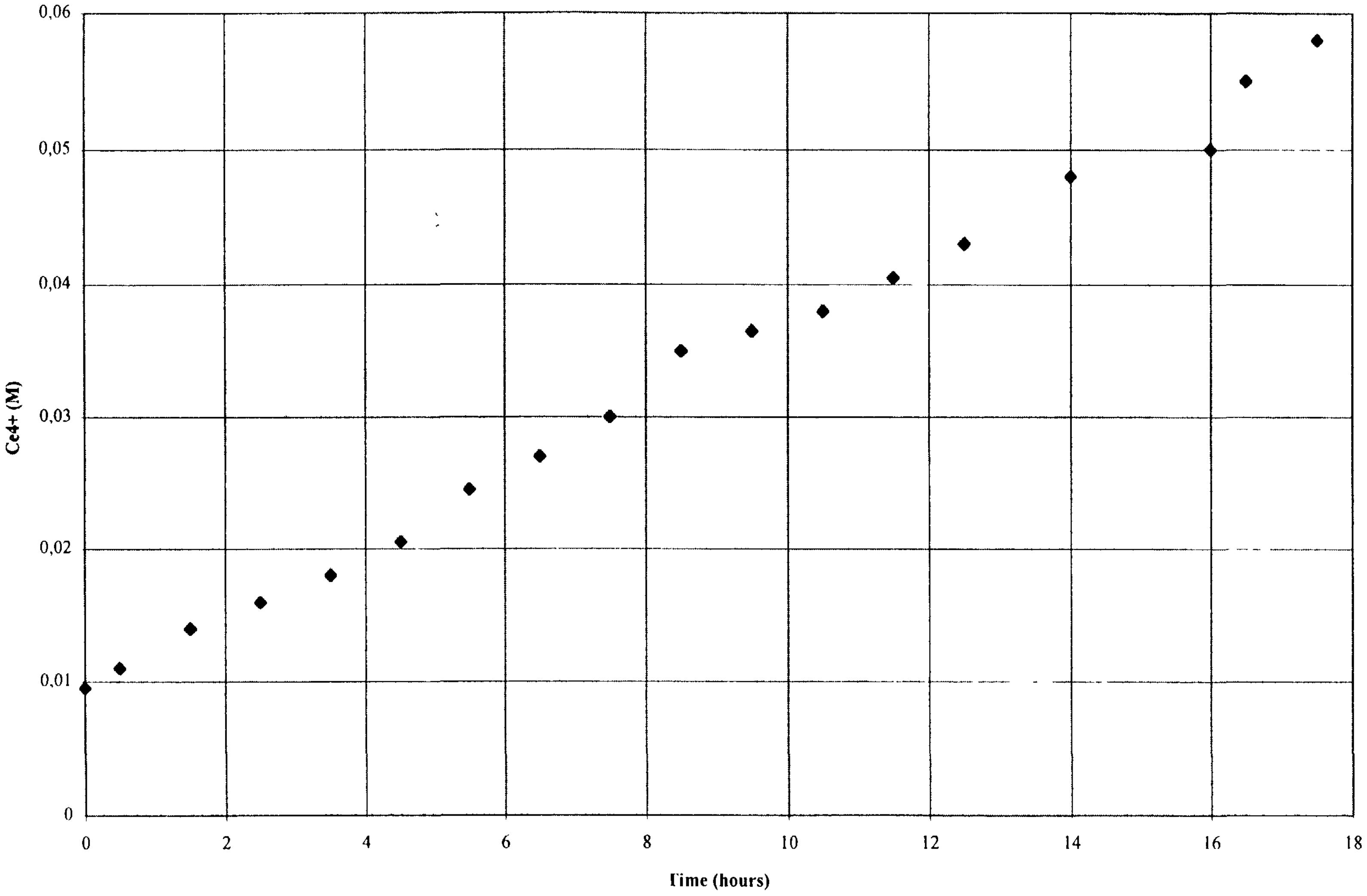


FIG. 3. Regeneration test at 80 °C.

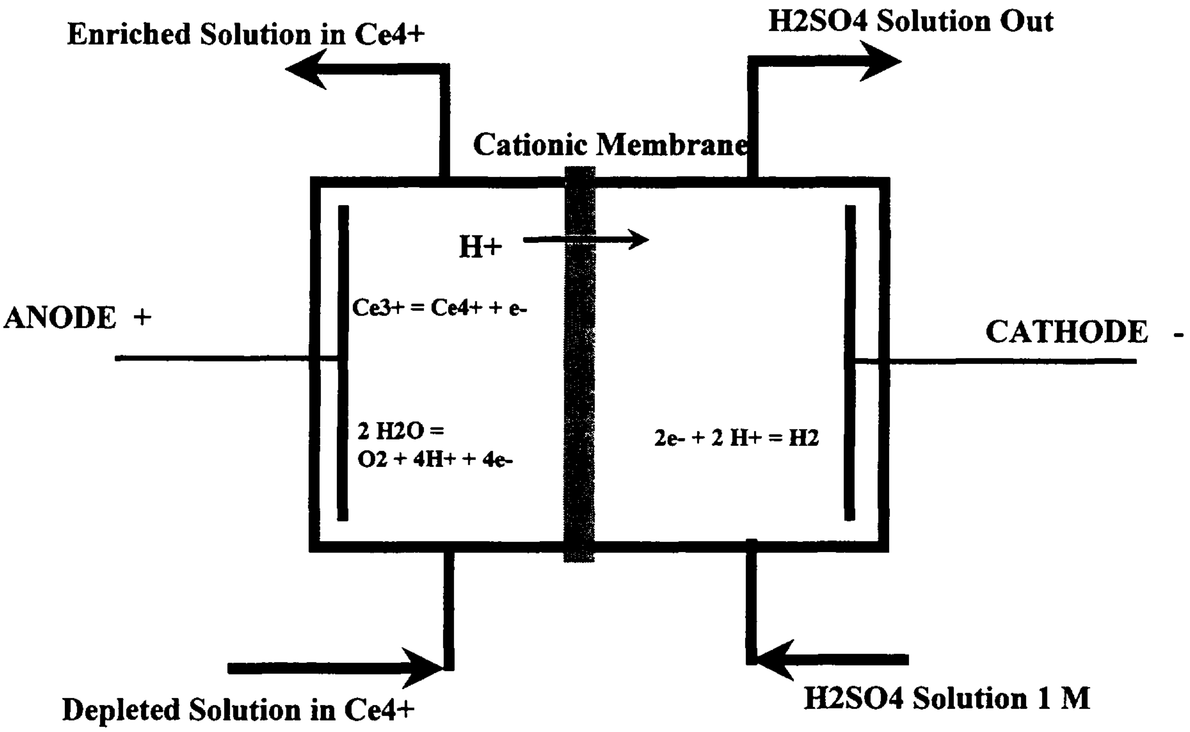


FIG. 4. Electrolytic regeneration of Cerium 4+.

One experiment comprises the following operations :

- prepare the loops by verifying they are dry; prepare adequate anolyte and catholyte solutions
- introduce known volumes of adequate anolyte and catholyte solutions into their respective loops
- circulate both fluids into the loops and adjust the temperature to the desired level
- turn on the electrolysis cell and adjust the current density to the desired constant value
- take samples (known volumes) at regular time intervals and measure the concentration of the ceric ion by titration with Fe^{2+}

Some experiments were carried out in the presence of ultrasonic waves to assess their influence on the diffusion layer (and on the double layer for we noted in the past that ultrasonic waves can also accelerate irreversible electronic transfers).

During any particular experiment, the selectivity decreases with increasing values of γ. This results from the diffusion control of the oxidation of Ce^{3+}. Indeed, the concentration of the cerous ion decreases progressively. If the initial concentration is high enough, the total steady-state current imposed by the operator can be supported by diffusion and the selectivity remains very high.

This, of course, depends also on the other variables like temperature and hydrodynamic conditions (thickness of the diffusion layer). With decreasing concentrations of the cerous ion, the concentration gradient in the diffusion layer reaches a critical value for which we may assume that $[Ce^{3+}]$ is about zero near the anode. From this point on, the diffusion is not able

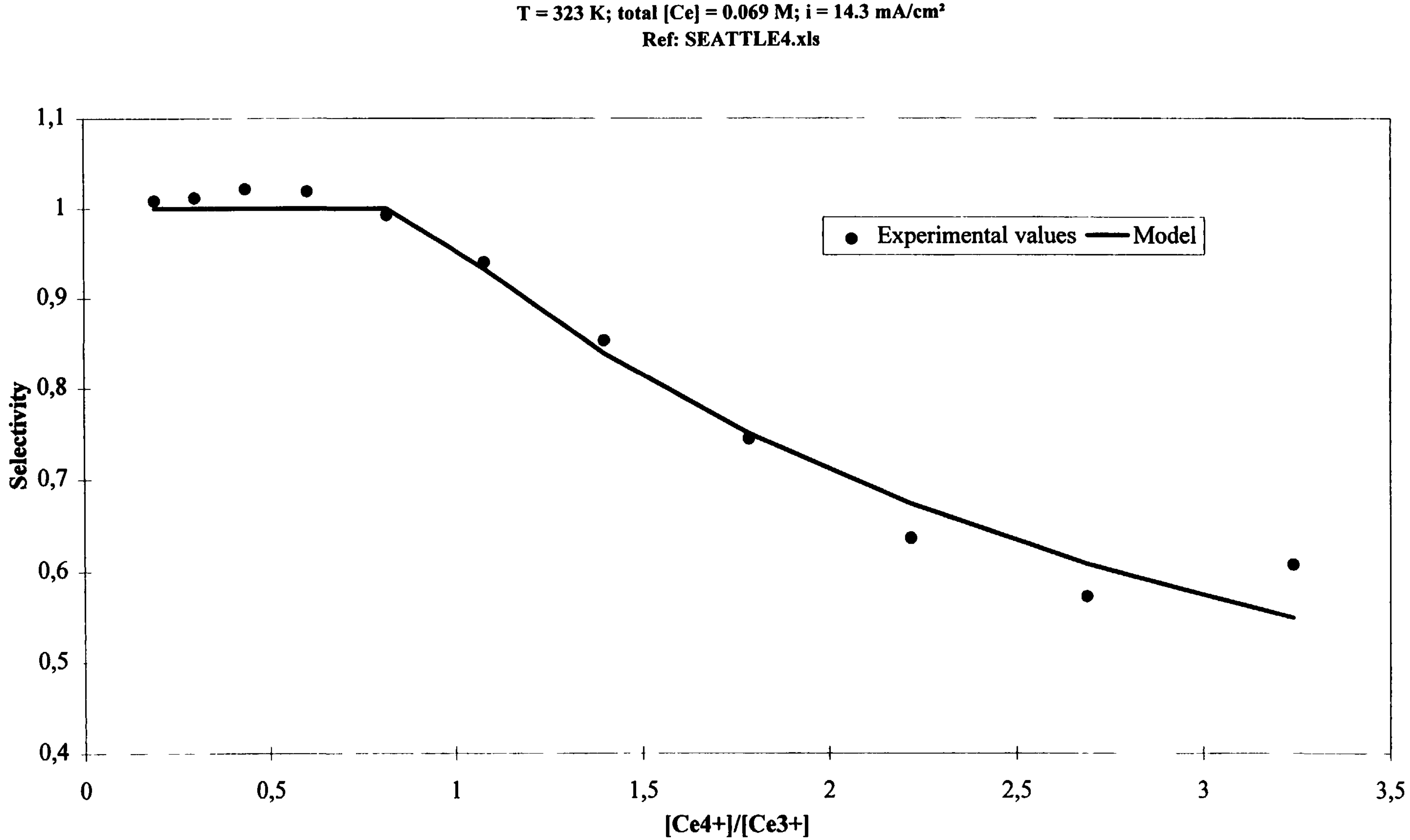


FIG. 5. Selectivity vs [Ce4=]/[Ce3=].

anymore to support the total current and the oxidation of water begins to play a non-negligible role. This explains the sudden decrease of the selectivity which is both observed experimentally and accounted for by the model.

Treatment of the data

The evolution of the concentration of the ceric ion in function of time allows to calculate the experimental transient value of the selectivity. For this purpose, the total effective charge transferred to the cerous ions is being divided by the total charge passed through the electrolyser. The change of the total volume as a result of the sampling has been taken into account but electro-osmotic effects have been provisionally neglected. Since the calculation of the selectivity is based on concentration differences, a preliminary smoothing of the measured Ce^{4+} concentration has been carried out to eliminate most of the experimental noise. This treatment has been made using the method of Savitzky and Golay [10]. Two groups of data have been considered in function of the temperature (50 °C and 80 °C). At this stage, we first calculated on the basis of literature data [12]. Next, we submitted each group of data to non linear fitting, using the NLREG code [13], thereby calculating the best estimates for χ and ν_1.

Results and discussion

Table IV gives the mean values for χ and ν_1. The radius of the 95 % confidence intervals at 50 °C are 2.6 (27 %) and 0.07 (9.8 %) for χ and ν_1 respectively. The model explains 91 % of the observed variance. Figure 5 allows to compare the theoretical predictions with the observed data.

Table IV : Fitted values for χ and υ_1

Experimental conditions	**χ(C.m.eq^{-1}.s^{-1})**	**υ_1**
50 °C without ultrasonic stimulus	9.6	0.71
80 °C without ultrasonic stimulus	13.9	0.71
50 °C with ultrasonic stimulus	10.8	0.71

According to the literature [8], the electrochemical oxidation of Ce^{3+} can be carried out on platinum electrodes with selectivities around 60-80 %. Our results indicate that higher selectivities can be reached if care is taken to choose the process variables adequately. We confirm that the selectivity is increased when operating at higher temperatures, lower current densities, lower $[Ce^{4+}]/[Ce^{3+}]$ ratios and more turbulent regimes. All these factors are favouring the selective oxidation of cerium. Next, we observe that ultrasonic waves can also increase the selectivity.

In the present case, the influence of ultrasonic waves is probably due mainly to micro-mechanical effects on the hydrodynamic conditions (the diffusion layer is decreased) though the impact of ultrasonic waves on the structure of the double layer also exists.

Selectivities as high as 95 % can be obtained. Further experiments using an FM01 electrolysis cell from ICI were carried out in an attempt to verify the possible industrial application of these results. It appeared that the standard Pt on Ti anode does not allow to obtain the same results. The high oxidative properties of the solution (sulphuric acid + ceric ion) led to peel off after a few hours while the highest selectivity was around 70 %. Since the thickness of the Pt layer on the standard electrode is around 10 µm, we think that the deposit is still porous (this would explain the observed peel off) and that the electro-active area may be smaller than the geometrical area. Another point of interest related to the thickness of the coating is that the corrosion rate of Pt is not zero. We measured the loss of weight of the anode in function of time and derived a corrosion rate equal to 4 nm/hour. The lifetime of the industrial electrolyser being approximately 3 years, we are now considering the possibility to manufacture a thick and non porous platinum coating on Ti. The final choice will essentially depend on the economical aspects.

8. DESIGN OF AN INDUSTRIAL SCALE CHEMICAL DECONTAMINATION UNIT

Finally, we selected the ozone process for the cerium solution regeneration based on economical as well as technical aspects.

The design of an industrial scale unit for the batch treatment of cutted pieces using the cerium process is in progress. The unit will comprise three main equipments:

- a chemical reactor operating at 80°C with loading of the pieces in a basket;
- a regeneration unit with ozone;
- a rinsing unit with ultrasonics.

The unit should start operation in 1998.

9. CONCLUSIONS

The main lessons drawn from this research programme are:

- the technical feasibility of the decontamination processes is proven at either technical scale or pilot scale,
- improvements are still needed mainly in the minimization of the secondary wastes,
- the economic aspect of the decontamination operation must be examined carefully; all aspects have to be taken into account (investment, operating costs, secondary waste)
- due to the continuous increase of the waste conditioning and disposal costs which is largely above the normal inflation rate, it is more and more economic to decontaminate,
- the procedures and techniques to prove that the pieces treated can be free released are of paramount importance; the politico-social aspects of the free release are also very important,
- the melting of metallic pieces in a nuclear foundry is very interesting : it can be used as a measurement process for the pieces of very low residual activity, as a decontamination technique and as a recycling technique in the nuclear world for the fabrication of shielding blocks, containers...

REFERENCES

[1] V. MASSAUT "Lessons learned during the BR3 European pilot decommissioning project", 5th International Conference on decommissioning of nuclear facilities, London, February 19-21, 1997

[2]J.DADOUMONT, V.MASSAUT, "The use of mechanical cutting techniques in the BR3-PWR decommissioning project". International conference on Cutting technology 1997 (ICCT'7); Hamburg March 5-6, 1997

[3]M.KLEIN et all, "Decontamination for dismantling:Full system decontamination and thorough decontamination of dismantled pieces", Int.Symposium on decontamination and decommissioning: Knoxville, Tennessee, USA, April 24-29, 1994.

[4]M.KLEIN, "Thorough decontamination of metallic pieces with the cerium process", 6th international SPECTRUM meeting on nuclear and hazardous waste management; Seattle, August 18-23, 1996.

[5]Y.DEMEULEMEESTER et all, "The management of the material flow by the dismantling of a nuclear reactor: approach and experience gained during the dismantling of the BR3 reactor." 3rd EU seminar on melting and recycling of metallic materials from decommissioning. Nykôping, Sweden, June 11-13, 1997.

[6]T. SUWA, N.KURIBAYASHI, E. TACHIKAWA, J. of Nucl. Sci. Technol., 23[7], 622 (1986)

[7]R. FUJITA, M. ENDA, T. MORISUE, J. of Nucl. Sci. Technol., 26[3],339 (1989)

[8]T. SUWA, N. KURIBAYASHI, E. TACHIKAWA, J. of Nucl. Sci. Technol,25[7] , 574 (1988)

[9]L. ANTROPOV, "Electrochimie Théorique", Mir Editions (1979)

[10]A. SAVITZKY, M. J. E. GOLAY, Anal.Chem., 36, 1627 (1964)

[11]J. STEINIER, Y. TERMONIA, J. DELTOUR, Anal. Chem., 44, 1909 (1972)

[12]J. P. HOARE, J. WILEY, "The Electrochemistry of Oxygen", pp82, Interscience NY (1968)

[13]NLREG, P. H. Sherrod, ASP Member, Personal communication (1995)

[14]A.RAHIER, M.KLEIN, M.PONNET, " Theoretical and experimental study of the selective oxidation of the cerous ion on a Pt-Ti anode in sulphuric acid solutions" Presented at the Barcelona Conference, 14-18 April 1997: "Electrochemical Processing-The versatile solution."

XA9847483

UV/OZONE TREATMENT TO DECONTAMINATE TRITIUM CONTAMINATED SURFACES

J.P. KRASZNAI, R. MOWAT
Ontario Hydro Technologies,
Toronto, Ontario,
Canada

Abstract

Tritium contamination on surfaces is often encountered during operation and maintenance of equipment at the Darlington Tritium Removal Facility and likely at other tritium handling facilities. The use of efficient decontamination techniques that produce little or no secondary wastes is desirable. At Ontario Hydro Technologies (OHT) we have been developing a process utilizing a combination of ultraviolet (UV) radiation and ozone gas to remove tritium surface contamination from materials often used in tritium service. This paper summarizes the performance of the technique. The results are encouraging because the technique is very effective, simple in terms of equipment requirements and concentrates tritium in an easily managed waste form.

I. INTRODUCTION

System components and tool surfaces when exposed to elemental tritium become contaminated. Some kind of rudimentary decontamination method is often necessary to permit maintenance to proceed safely, to replace tools into storage or to safely transport items from the station to non radioactive facilities for testing or repairs. Decontamination techniques available in the field include water/steam cleaning and desorbing tritium species by heating the part requiring cleaning/1,2/. Glow discharge cleaning which makes use of the kinetic energy of ionized gas energized by the passage of a radiofrequency discharge through the gas is used in the semi conductor industry and by the magnetic fusion R&D community. A workstation based on this technique to decontaminate tritiated surfaces has been developed at OHT/3,4/.

There is convincing evidence/5/, that all surfaces exposed to the environment quickly become contaminated with organic species. These are very common in the atmosphere due to the extensive use of hydrocarbon based materials in modern society. When these surfaces are subsequently exposed to elemental tritium, the surface organic contamination becomes tritiated. Surface organic contamination is a common problem in the semiconductor industry. A technique used to clean silicon wafers used in circuit boards is to expose them to ultraviolet radiation in the presence of oxygen/6,7/. The application of UV/ozone to decontaminate tritium contaminated surfaces however has not been tried before.

This paper summarizes the performance of the technique for stainless steel, the most commonly used material in tritium service. Some information on the effectiveness of the technique for other materials both metallic and non metallic is also provided. The objective of the work described here was to answer the following questions:

(1) What kind of decontamination factor (DF) can be expected from the process?

(2) Is the rate of tritium removal fast enough to be of practical use at tritium handling facilities?

(3) What are the important parameters that need to be looked at in detail to make the technique field applicable?

II. HOW DOES THE TECHNIQUE WORK?

Figure 1 is a schematic representation of how the technique works for surfaces contaminated by organic species.

The UV radiation source emits two wavelengths of light. The 254nm wavelength is strongly absorbed by organic molecules and they break down to smaller molecular weight reactive species. The shorter wavelength light at 185nm is absorbed by oxygen in air and generates ozone which then reacts with the organic species generated by the 254nm photons to produce volatile species such as CO_2, methane and water. If the surface is also contaminated by tritium then these volatile products will also incorporate tritium, effectively decontaminating the surface. In a successful process however it is also necessary to ensure that the tritium removed will not be available to recontaminate the surface.

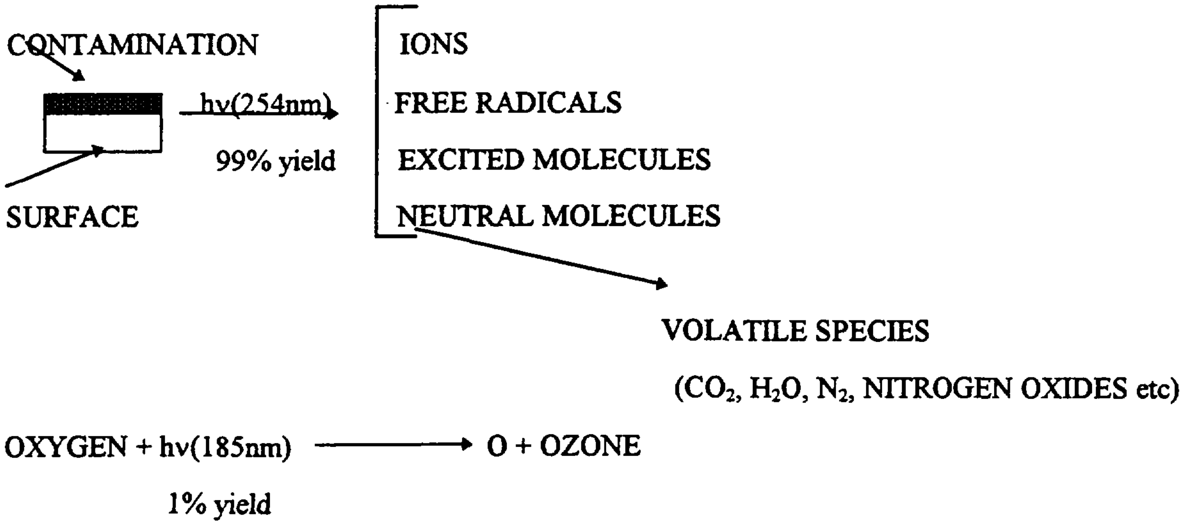


Figure 1 Schematic of UV/Ozone Decontamination Process

Advantage of the Technique

The UV/ozone technique operates at room temperature and pressure and therefore does not require a vacuum system. Because conditions in the UV cell are highly oxidizing the tritium species that desorb from a contaminated surface are expected to be oxidized and trapped on a solid polar absorbent such as molecular sieves or silica gel resulting in a small quantity of manageable solid waste.

The technique is not limited to cleaning exterior surfaces. Previous work/6/ has shown that interior surfaces not directly accessible to UV radiation can also be cleaned because of the accessability of ozone gas to the contamination site. A very exciting possibility is the transmission of UV radiation through a fiber optic cable to decontaminate inaccessible internal surface of a container or piping/valve system.

EXPERIMENTAL

A Rayonet photochemical reactor containing 16 individual UV lamps in a cylindrical arrangement was used in these tests. A 5.5cm UV transparent quartz cell with the tritium contaminated specimen inside it was placed in the center of the reactor.

Stainless steel coupons with three surface finishes were used in the decontamination trial. Four coupons had a 4B (standard matte) finish, two were mirror finished and two were electropolished. All the coupons were washed prior to tritium contamination with deionized (DI) water and acetone and air dried following rinsing in ethanol. The coupons were exposed to elemental tritium at a pressure of 370 torr for 1hr and stored in an atmosphere of dry nitrogen gas until used in the experiments. Each coupon was suspended inside the quartz cell by a length of steel wire. The tritium removed from the coupon was carried in a flow of humid air (80-90mL/min) to a series of traps where the exchangable tritium was removed from the gas flow. The air, free of exchangable tritium species then passed over heated copper oxide at 750°C, where the remaining tritium is oxidized before being trapped in the second series of water traps. The schematic of the equipment used is shown in Figure 2.

The amount of tritium remaining on the specimen following decontamination was determined by heating it at 120°C initially and then at 1000°C for at least 6 hrs and collecting the desorbed tritium in a series of water traps as described above. Samples from these were then counted by liquid scintillation. A Scintrex tritium in air monitor measured the exhaust air from the last water trap to ensure that all of the tritium associated with the specimen would be accounted for. Our previous experience suggested that most of the tritium is desorbed from a tritium contaminated specimen at 120-150°C with a smaller amount desorbed at higher temperatures. One steel specimen was digested in nitric acid/hydrochloric acid (1:3) to ensure all the tritium was removed after 6hours at 1000°C.

Tritium plateout on the equipment surfaces was minimized by the use of humid air as the purge gas during thermal desorption. After the second experiment it became clear however that the rate of desorption of tritiated species from the specimens exceeded the rate at which they could be purged from the UV cell even by using humid air. The experimental protocol was subsequently changed by incorporating silica gel at the bottom of the UV cell to absorb the tritiated species. These were then leached in DI water toextract and determine the tritium by LSC. To further ensure that all of the desorbed tritium was accounted for, the apparatus was dismantled after each test and each component was washed in deionized water which was then counted by liquid scintillation method. This procedure, we believe accounted for all tritium associated with the specimens.

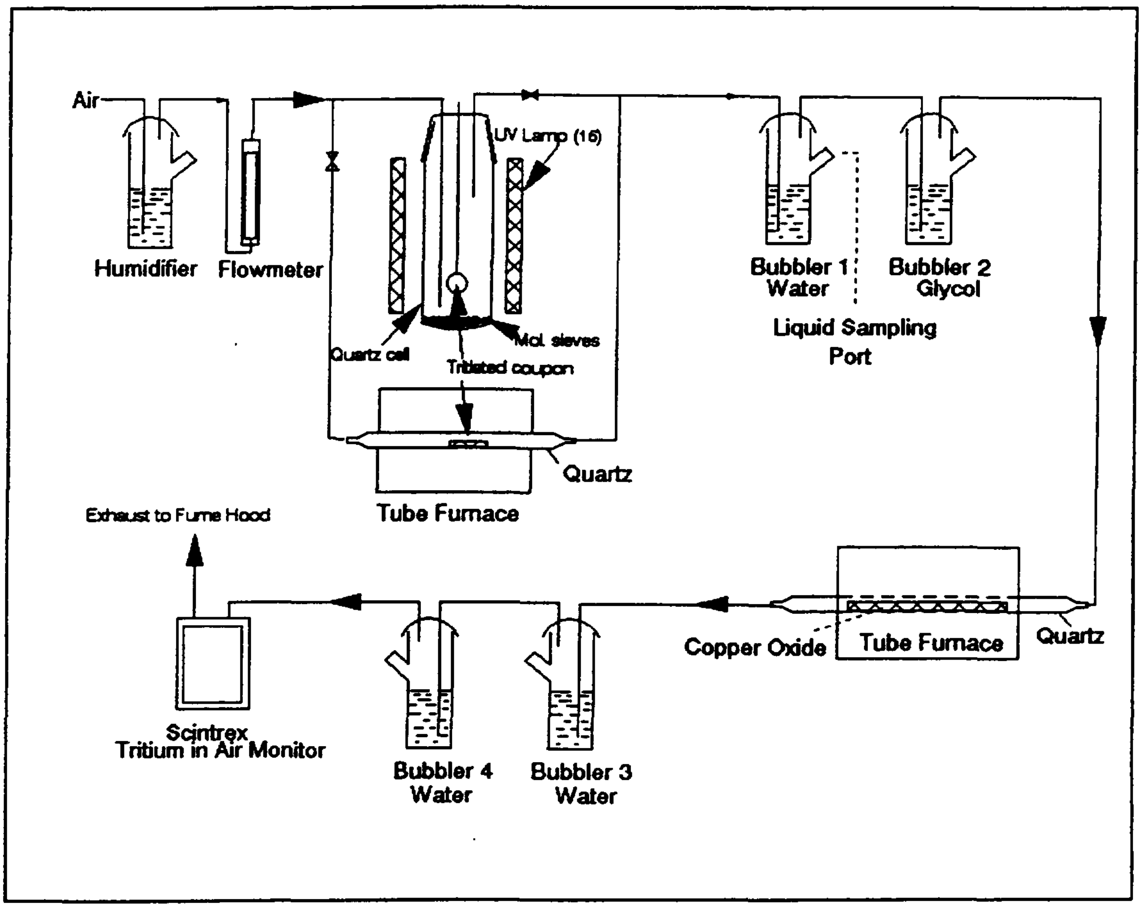


Figure 2 Schematic of UV/Ozone Equipment

EFFECT OF SURFACE FINISH

The inventory of tritium in each specimen was determined at the end of each experiment by summing the residual tritium thermally desorbed at 1000°C, the tritium leached from the silica gel and the equipment washings. Each specimen type was run in duplicate and Table 1 summarizes the inventory results. The inventory decreases in the order as-received > mirror finish > electropolished. This observation is consistent with the expectation based on surface area arguments that the smoother the surface the less tritium (or other contamination) that the surface will adsorb. Although the tritium inventory varied by a factor of two the effectiveness of the decontamination technique was very similar for each surface finish indicating that the nature of the contamination rather than its quantity determines the effectiveness of the technique.

TABLE 1

TRITIUM INVENTORY OF STAINLESS STEEL SPECIMENS

316L SS COUPON	SPECIFIC ACTIVITY (MBq/cm^2)±STD.DEV	TOTAL TRITIUM (MBq)
4B FINISH	5.2±0.4	45±3
MIRROR FINISH	4.1±0.7	35±6
ELECTROPOLISHED	2.9±0.4	25±3

EFFECT OF UV EXPOSURE TIME

As Figure 3 illustrates, the degree of tritium removal depends on the exposure time. The tritium removal efficiency however decreases with time perhaps as a result of less volatile and more oxidation resistant tritiated species being present at the longer periods. At least 6 hours of exposure was required to remove approximately 94% of the total tritium.

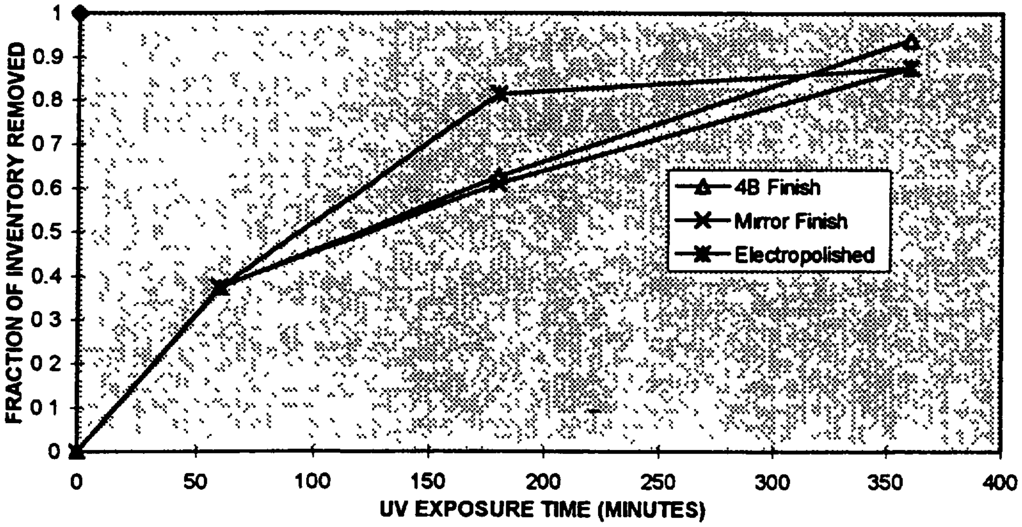


Figure 3 Decontamination Effectiveness as a Function of UV Exposure Time

EFFECT OF OXYGEN

The relative efficiency of UV and ozone in removing tritiated species was determined by substituting nitrogen gas for oxygen. As the data in Table 2 indicates the decontamination effectiveness is greatly reduced when oxygen is absent. This is very important from the point of view of tritium removal from inaccessible locations using this technique. Fiber optic technology at the present time does not permit the transmission of the 185nm wavelength of light necessary to produce ozone in situ.

EFFECT OF DISTANCE FROM UV SOURCE

The distance from the specimen to the UV source was of the order of 10cm. The literature indicates that the closer the contaminated specimen is to the UV source the faster it can be contaminated. The reason for this is that the ozone generated by the UV lamp itself absorbs at 260nm, the same wavelength as the organics on the specimens. Therefore the more ozone between the specimen and the UV lamp the less 254nm radiation can reach the contaminated specimen surface. The optimum distance of the UV lamp to the specimens needs to be established in future work taking into consideration the need to ensure that the tritium removed from the component to be cleaned does not "plate" out on surfaces close to the component resulting in recontamination and a less effective decontamination than desired.

EFFECTIVENESS ON OTHER MATERIALS

The technique was applied to a number of non metallic materials which were contaminated by tritium. The results which proved disappointing are shown in Table 3. The average decontamination factor obtained after exposing the specimens to UV/oxygen for 6 hours ranged from a high of 62% for tritiated borosilicate glass to 10% for EPDM rubber.

TABLE 2

The Effectiveness of Nitrogen and Oxygen with 6hr UV Exposure.

COUPON	CELL GAS	EFFICIENCY
1	AIR	93.5%
2	AIR	93.3%
3	AIR	94.3%
4	NITROGEN	46.2%
5	NITROGEN	31.3%
6	NITROGEN	38.2%

TABLE 3

Effectiveness of UV/Ozone Technique for Various Materials

MATERIAL	PERCENT TRITIUM REMOVED
STAINLESS STEEL	94
BOROSILICATE GLASS	62
HIGH DENSITY POLYETHYLENE	35
POLYCARBONATE	57
EPDM RUBBER	10
NEOPRENE RUBBER	13
VITON	12
TEFLON	52

The reasons for the relatively poor decontamination factors (DFs) is likely to be a combination of increased porosity of the materials allowing tritium to diffuse further into the material and the reaction of oxygen/ozone in the presence of UV with the organic substrate.

CONCLUSIONS

The effectiveness of the decontamination is dependent on the duration of the UV exposure.

A 6 hour UV/ozone exposure of tritiated stainless steel coupons was successful in removing 94% of the total tritium inventory. Removal of the remaining 6% is more difficult likely because the residual tritiated species are more resistant to oxidation. This rate of decontamination is practical for small parts and tools that can be placed in an oven type arrangement and left overnight for cleaning.

For a given UV exposure period the data indicates that the effectiveness of the decontamination does not depend on the surface finish.

The use of a dessicant in the proximity of the specimen was beneficial in preventing recontamination. In a practical decontamination system fast flowing air is likely to be more efficient at preventing recontamination. This needs to be confirmed.

These tests used flat stainless steel discs. In actual field use more complex geometries will be encountered. Future effort should include actual specimens from the TRF.

The technique is not effective for non metallic materials probably because of the greater diffusivity of the tritium and the fact that the UV photons only interact with surface species.

ACKNOWLEDGEMENTS

The financial assistance of Ontario Hydro Nuclear-Darlington Generating Station is gratefully acknowledged.

REFERENCES

1. Wong, K.Y., Hircq, B., Jalbert, R.A., Shmayda, W.T., Fusion Engineering and Design, Vol.16 pp 159, (1991).

2. Krasznai, J.P. and Shmayda, W.T., "Decontamination Tests on Stainless Steel Tubing Removed from the Darlington Tritium Removal Facility", Ontario Hydro Research Division Report No.90-100-K (1990).

3. Antoniazzi, A.B., Shmayda, W.T., and Fishbein, B.F., "Design of a Tritium Decontamination Workstation Based on Plasma Cleaning", Ontario Hydro Research Report No. 93-19-K April 1993.

4. Antoniazzi, A.B., Shmayda, W.T., Proceedings of Tritium Technology in Fission, Fusion and Isotopic Applications Conference, Albuquerque, 1991, Fusion Technology 21(2) pp. 867 (1992).

5. Antoniazzi, A.B., Agg, P., Fishbein, B., Krasznai, J.P., Massey, R.E., and Mowat, R., Proceedings of Tritium Technology in Fission, Fusion and Isotopic Applications Conference, Belgirate, 1995, Fusion Technology (To be published.)

6. McIntyre, N.S., Davidson, R.D., Walzak, T.L., Williston, R., Westcott, M. and Pekarsky, A. "Uses of Ultraviolet/ozone for Hydrocarbon Removal: Applications to Surfaces of Complex Composition or Geometry", J. Vac. Sci. Technol. A9 (3) pp1355 (1991)

7. Vig, J.R., "UV/Ozone Cleaning of Surfaces" J. Vac. Sci. Technol. A3 (3) pp1027 (1985).

LOOP CLEANUP WITH REDOX DECONTAMINATION TECHNIQUE

XIAN WEN REN, YUAN ZHANG
China Institute for Radiation Protection,
Taiyuan, Shanxi,
China

XA9847484

Abstract

The corrosion rate of stainless steel in nitric acid solution will be enhanced by existence of Ce^{4+}. The nitric acid solution containing Ce^{4+} is an effective chemical decontamination technique to contaminated stainless steel by radioactive nuclides. In order to reduce the decontamination cost and the volume of waste liquid, the Ce^{3+} coming from the reduction of Ce^{4+} following reacting with metal should be re-oxidized into Ce^{4+}, then it can be recycled and reused to act with contaminated surface of stainless steel.

The goal of this study is to develop a circular decontamination process in medium of nitric acid, in order to use it in a loop clean up. That needs a specially designed electrolytic cell to oxidize the Ce^{3+} into Ce^{4+}. This regenerator's structure should be simple and easy to operate, and can meet the requirements of practical decontamination operation.

The concentration of Ce^{4+} in the nitric acid solution was selected to provide a suitable corrosion rate to contaminated stainless steel. The total concentration of cerium (III+IV) was also optimized to ensure that the regeneration rate of Ce^{4+} could satisfy the consumption rate of Ce^{4+} during decontaminating process. The operation parameters were selected strictly on the basis of our experimental results, so that the regeneration rate of Ce^{4+} can be higher reasonably in proper operation conditions and not arise any problem related to safety of operation and nuclear aspects.

It is considered that this decontamination process could be applied into either decommissioning or maintenance stage of nuclear facilities.

The concentration of Ce^{4+} and temperature are the main factors for corrosion rate, other factors should also be considered during decision of decontamination process. With the regenerator developed under contract No 7959/RB could obtain sufficient decontamination factors, when use following conditions: concentration of Ce^{4+} is higher than 0.2 mol/l, the total concentration of cerium (III + IV) is higher than 0.4 mol/l, concentration of nitric acid is higher than 2 mol/l, temperature of decontamination operation is within 25°C – 40°C and temperature of regeneration is within 40°C – 50°C.

1 INTRODUCTION

Decontamination of stainless steel contaminated with radionuclides is difficult to meet the requirement of regulations. When Ce^{4+} exists in acidic solution, the corrosion rate of stainless steel will be increased obviously. A thin surface layer of contaminated stainless steel will be removed rapidly within a few hours, and the contaminants adhered strongly on the surface will also be removed into the decontamination solution, therefore, higher decontamination factors (DFs) could be obtained. This decontamination technique has already be used in batch scale decontamination. Since the Ce^{4+} will be reduced into Ce^{3+} during the decontamination process following its reaction with the metals or metal oxides, the DFs will become lower and lower, so it is difficult to be used in loop clean up. In order to do that, you need to put additional new Ce^{4+} into the decontamination solution or to re-oxidize the Ce^{3+} to Ce^{4+}. Research Contract 7959/RB conducted by China Institute for Radiation Protection tries to develop a chemical decontamination process of nitric acid - Ce^{4+}. According to the development programme, research contents will involve: corrosion behaviors of stainless steel; feasibility investigation of single cell regenerator; corrosion behaviors of Ce^{4+} regenerated by the single cell regenerator; demonstrative clean up of stainless steel loop with this decontamination process.

We choose electrochemical method and the single cell regenerator as the means to reoxidize Ce^{3+}, because it could get higher regeneration rate to meet the requirements of effective decontamination, no other harmful materials to enter the decontamination solution and less volume of waste liquid to be produced from the decontamination process.

2 BACKGROUND AND OBJECTIVES OF THE RESEARCH PROJECT

Evans,T. E. discovered that corrosion rate of stainless steel would be enhanced with existence of some inorganic oxidation – reduction ions, for example Cr^{6+} / Cr^{3+} in 1956. Lerch, R. E. used Ce^{4+} / Ce^{3+} to replace Cr^{6+} / Cr^{3+} to do the same experiment in 1968. Partridge, J. A. et al approached the feasibility of decontamination using this reaction and of regeneration of Ce^{4+} with electro-reoxidizing process in 1979. Later of 1980' Japan Institute of Atomic Energy performed a decontamination of main cycle of reactor using Ce^{4+} - H_2SO_4 solution and results showed that this method could get high DFs, speed of this reaction was sufficient fast, good dissolution capacity for metals and oxides and decontamination agent could be regeneration by electrolyzing. After that time, membrane regenerator and single cell regenerator were developed, but all of those could only provide limited regeneration capacity and not be used in real decontamination process. This research project tries to develop a nitric acid – Ce^{4+} decontamination process with electrochemical regeneration of Ce^{4+} and to be used into loop clean up. If it is success, this decontamination technique will mainly be used in decommissioning of nuclear facilities.

3 TECHNICAL APPROACH

This research project will involve following contents: corrosion behaviors of stainless steel, feasibility investigation of regeneration of Ce^{4+} with single cell regenerator in medium of nitric acid , regenerator designing, test and improvement, corrosion behaviors of Ce^{4+} regenerated by the single cell regenerator, demonstrative clean up with this decontamination process. All of those research contents will be conducted in four stages.

4 ACCOMPLISHMENTS

4.1 Corrosion Rates of Stainless Steel

Corrosion rates of 1Cr18Ni9Ti stainless steel were measured in order to get information of the behaviors of Ce^{4+} in nitric acid solution. Those data will be used as a baseline to compare with that of Ce^{4+} regenerated.

4.1.1 Effects of Concentration of Nitric Acid on Corrosion Rates

When temperature of the decontamination solution is 80°C and the concentration of Ce^{4+} is 0.2 mol/l, the effects of concentration of nitric acid to the corrosion rates of stainless steel are listed in Table I. The results show that there is a sudden change, when concentration of nitric acid is higher than 1.5 mol/l. That means that 2 mol/l will be the lowest concentration of nitric acid to obtain good DFs.

Table I Effects of HNO_3Concentration on Corrosion Rates

$[HNO_3]$,mol/l	1.0	1.5	2.0	3.0	4.0	6.0
	1.2	3.1	14.6	15.2	15.5	16.0

4.1.2 Effects of Operation Temperature on Corrosion Rates

When concentration of nitric acid is 2 mol/l and concentration of Ce^{4+} is 0.2 mol/l, the effects of operation temperature to corrosion rates are listed in Table II. The results show that operation temperature appears great affection to the corrosion rates. When operation temperature is 30°C, surface of the stainless steel could be removed 90¦Ìm / hr.

Table II Effects of Operation Temperature on Corrosion Rates

T, °C	30	40	50	60	70	80
	0.7	1.5	3.2	6.3	9.8	14.5

4.1.3 Effects of Concentration of Ce^{4+} on Corrosion Rates

When operation temperature remains at 80°C and concentration of HNO_3 is 2 mol/l, the concentration of Ce^{4+} in decontamination solution has important effect to corrosion rate of stainless steel. The data listed in Table III show that sufficient corrosion rates could be obtained even the concentration of Ce^{4+} is as low as 0.03 mol/l, but at higher temperature, the low concentration of Ce^{4+}could cause much rougher surface.

Table III Effects of Concentration of Ce^{4+} on Corrosion Rates

$[Ce^{4+}]$, mol/l	0.03	0.05	0.15	0.20	0.30	0.40
	2.3	5.1	10.2	14.5	17.8	20.5

The results of electron diffraction on the surface of stainless steel to have been decontaminated discovers that the Ce^{4+} reacted mainly with the surface of crystal grain of stainless steel and the HNO_3 acted mainly with the crystal edge. So that, with the increase of concentration of Ce^{4+} the surface of stainless steel to be decontaminated will become much smoother and high concentration of HNO_3 will make crystal grain more clear.

4.2 Feasibility Investigation of Regeneration of Ce^{4+} in HNO_3 Solution with Single Cell Regenerator

The single cell regenerator will make the electrode reaction very complicated. The main electrode reactions are listed in Table IV. If the single cell regenerator could remain the reactions of H^+ / H_2 and Ce^{4+} / Ce^{3+} as the main reactions, new Ce^{4+} will be obtained from the regeneration. The total reaction rate in the cell can be expressed as:

$Q_t = 3600 I / F * S_a$

There, I is the total current density [A/cm^2], F is Faraday constant (96500 C/mol), S_a is the anode surface area [cm^2].

The regeneration rate of Ce^{4+} can be calculated with following formula:

$Q_{Ce(4+)} = ([Ce^{4+}]_a - [Ce^{4+}]_b) * V_s / T * S_a$

There, $Q_{Ce(4+)}$ is the regeneration rate of Ce^{4+} by the regenerator [$mol/cm^2 .hr$]

$[Ce^{4+}]_a$ is the concentration of Ce^{4+} in decontamination solution after regeneration [mol/l]

$[Ce^{4+}]_b$ is the concentration of Ce^{4+} in decontamination solution before regeneration [mol/l]

V_s is the volume of decontamination solution, [L]

T is the time duration of regeneration, [hr]

S_a is the surface area of anode, [cm^2]

The current efficiency for regeneration of Ce^{4+} will be ¦Ç$= Q_{Ce(4+)} / Q_t$

Table IV Electrode Reaction and Their Standard Electrode Potentials

No.	Electric couple	Electrode reaction	Standard potential(V)
1	Ni^{2+} / Ni	$Ni^{2+} + 2e \_ Ni$	-0.23
2	Fe^{3+} / Fe	$Fe^{3+} + 3e \_ Fe$	-0.03
3	H^+ / H_2	$2H^+ + 2e \_ H_2$	0.00
4	SO_4^{2-} / H_2SO_4	$SO_4^{2-} + 4H^+ + 2e \_ H_2SO_4 + H_2O$	0.20
5	Fe^{3+} / Fe^{2+}	$Fe^{3+} + e \_ Fe^{2+}$	0.77
6	NO_3^- / NO_2	$NO_3^- + 2H^+ + e \_ NO_2 + H_2O$	0.79
7	NO_3^- / N_2O_4	$2NO_3^- + 4H^+ + 2e \_ N_2O_4 + 2H_2O$	0.81
8	NO_3^- / HNO_2	$NO_3^- + 3H^+ + 2e \_ HNO_2 + H_2O$	0.94
9	NO_3^- / NO	$NO_3^- + 4H^+ + 3e \_ NO + 2H_2O$	0.96
10	O_2 / H_2O	$O_2 + 4H^+ + 4e \_ 2H_2O$	1.23
11	$Cr_2O_7^{2-} / Cr^{3+}$	$Cr_2O_7^{2-} + 14H^+ + 6e \_ 2Cr^{3+} + 7H_2O$	1.33
12	Ce^{4+} / Ce^{3+}	$Ce^{4+} + e \_ Ce^{3+}$	1.44
13	NiO_2 / Ni^{2+}	$NiO_2 + 4H^+ + 2e \_ Ni^{2+} + 2H_2O$	1.93
14	$S_2O_8^{2-} / SO_4^{2-}$	$S_2O_8^{2-} + 2e \_ 2SO_4^{2-}$	2.00

The feasibility investigation was performed in a cone bottle of 1000 cm^3 worked as the single regeneration cell. A platinum plate of 3¡Á5¡Á0.05 cm acted as the positive electrode with area of 30 cm^2, and a platinum wire of ¦µ1¡Á15 mm acted as the negative electrode with area of 0.5cm^2. The area ratio of anode to cathode was 60 and the distance between the two electrodes was 30 mm.

4.2.1 Effects of Voltage on Current Density of Anode

When temperature is 25°C, 45°C and 70°C, using the apparatus mentioned above, the effects of voltage between the two electrodes on the anode currency were investigated in 2 mol/l of HNO_3 solution containing 0.05 mol/l of Ce^{3+} . The results are given in Table V. The results show that higher temperature needs lower voltage to achieve the same anode current density. The largest gap of the voltage is about 0.5V for 25°C and 70°C.

Table V Effects of Voltage and Temperature on Anode Current Density

	Current density,mA/cm^2	3.3	6.7	13.3	20.0	26.7
25°C	Electrode voltage, V	2.0	2.3	3.0	3.4	3.7
45°C	Electrode voltage, V	1.9	2.2	2.8	3.2	3.6
70°C	Electrode voltage, V	1.8	2.1	2.5	3.0	3.4

4.2.2 Effects of Temperature on Regeneration Rates of Ce^{4+}

When original concentration of Ce^{3+} was 0.05 mol/l in HNO_3 of 2 mol/l, using the apparatus mentioned above to investigate the effects of operation temperature on regeneration rate of Ce^{4+}. The results listed in Table VI show that when the anode current density is higher than 7 mA/cm^2, higher anode current density has no effects on regeneration rates of Ce^{4+}, but 13 mA/cm^2 seems more sensitive. Higher temperature could produce higher regeneration rate.

4.2.3 Effects of Convective Status on Regeneration Rates of Ce^{4+}

When operation temperature was 45°C, concentration of Ce^{3+} and Fe^{3+} were 0.05 mol/l respectively, using the apparatus mentioned above to investigate the effects of convective status to regeneration rates of Ce^{4+}. The results are showed in Table VII. It reveals that convection plays important action when the anode current density is lower, but for higher anode current density, it is no obvious effect for increasing the regeneration rate of Ce^{4+} .

Table VI Effects of Temperature on Regeneration Rates of Ce^{4+}

	Current density, mA/cm^2	3.3	6.7	13.3	20.0	26.7
25°C	$Q_{Ce(4+)}$, mM/cm^2*hr	0.114	0.192	0.186	0.180	0.180
45°C	$Q_{Ce(4+)}$, mM/cm^2*hr	0.114	0.240	0.252	0.246	0.246
70°C	$Q_{Ce(4+)}$, mM/cm^2*hr	0.114	0.234	0.372	0.312	0.300

Table VII Effects of Convective Status on Regeneration Rates of Ce^{4+}

	Current density, mA/cm^2	3.3	6.7	13.3	20.0	26.7
Stir	$Q_{Ce(4+)}$, mM/cm^2*hr	0.114	0.210	0.210	0.180	0.174
No	$Q_{Ce(4+)}$, mM/cm^2*hr	0.066	0.078	0.120	0.150	0.144

4.2.4 Effects of Concentration of Ce^{3+} on Regeneration Rates of Ce^{4+}

From above experimental results, it was surmised that the electrode reaction Ce^{3+} _ Ce^{4+} + e is controlled by the rate of mass transferring. That means the regeneration rate is related to the concentration of reactants. When operation temperature was 25°C and concentration of HNO_3 was 2 mol/l, using the same apparatus to investigate the effects of concentration of Ce^{3+} to regeneration rates of Ce^{4+}. The results listed in Tables VIII and IX show that the concentration of Ce^{3+} plays an effective role for increasing the regeneration rate of Ce^{4+}, especially when the anode current density is higher.

Table VIII Effects of Concentration of Ce^{3+} on Regeneration Rates of Ce^{4+} (25°C)

	Current density, mA/cm^2	3.3	6.7	13.3	20.0	26.7
[Ce^{3+}]:0.05M	$Q_{Ce(4+)}$, mM/cm^2*hr	0.120	0.186	0.186	0.180	0.180
[Ce^{3+}]:0.10M	$Q_{Ce(4+)}$, mM/cm^2*hr	0.120	0.240	0.390	0.402	0.420
[Ce^{3+}]:0.20M	$Q_{Ce(4+)}$, mM/cm^2*hr	0.120	0.240	0.486	0.612	0.606

Table IX Effects of Concentration of Ce^{3+} on Regeneration Rates of Ce^{4+} (70°C)

	Current density, mA/cm^2	3.3	6.7	13.3	20.0	26.7
[Ce^{3+}]:0.05M	$Q_{Ce(4+)}$, mM/cm^2*hr	0.114	0.228	0.378	0.318	0.306
[Ce^{3+}]:0.10M	$Q_{Ce(4+)}$, mM/cm^2*hr	0.114	0.246	0.486	0.708	0.738
[Ce^{3+}]:0.20M	$Q_{Ce(4+)}$, mM/cm^2*hr	0.120	0.234	0.492	0.492	0.300

4.2.5 Effects of Existence of Fe^{3+}, Ni^{2+} and $Cr_2O_7^{2-}$ on Regeneration Rates of Ce^{4+}

With the progress of the decontamination process, the contents of Fe^{3+}, Ni^{2+} and $Cr_2O_7^{2-}$ will increase gradually. Those ions might be reduced on the surface of cathode and the products could react with Ce^{4+}. So that, the total Ce^{4+} would descend. Experimental results listed in Table X, Table XI, Table XII, Table XIII, Table XIV and Table XV show that the regeneration rates would be reduced by existence of those ions, especially in lower operation temperature. So decontamination solution cannot be reused to have no limits.

Table X Effects of Fe^{3+} on Regeneration Rates of Ce^{4+} (25°C)

	Current density, mA/cm^2	3.3	6.7	13.3	20.0	26.7
[Fe^{3+}],0.00mol/l	$Q_{Ce(4+)}$, mM/cm^2*hr	0.120	0.186	0.186	0.180	0.180
[Fe^{3+}],0.05mol/l	$Q_{Ce(4+)}$, mM/cm^2*hr	0.120	0.168	0.168	0.150	0.150
[Fe^{3+}],0.20mol/l	$Q_{Ce(4+)}$, mM/cm^2*hr	0.060	0.108	0.090	0.078	0.072

Table XI Effects of Fe^{3+} on Regeneration Rates of Ce^{4+} (70°C)

	Current density, mA/cm^2	3.3	6.7	13.3	20.0	26.7
[Fe^{3+}],0.00mol/l	$Q_{Ce(4+)}$, mM/cm^2*hr	0.120	0.228	0.378	0.324	0.312
[Fe^{3+}],0.05mol/l	$Q_{Ce(4+)}$, mM/cm^2*hr	0.114	0.198	0.312	0.306	0.270
[Fe^{3+}],0.20mol/l	$Q_{Ce(4+)}$, mM/cm^2*hr		0.078	0.138		0.264

Table XII Effects of Ni^{2+} on Regeneration Rates of Ce^{4+} (25°C)

	Current density, mA/cm^2	3.3	6.7	13.3	20.0	26.7
[Ni^{2+}],0.00mol/l	$Q_{Ce(4+)}$, mM/cm^2*hr	0.120	0.186	0.180	0.174	0.174
[Ni^{2+}],0.05mol/l	$Q_{Ce(4+)}$, mM/cm^2*hr	0.120	0.189	0.180	0.180	0.180

Table XIII Effects of Ni^{2+} on Regeneration Rates of Ce^{4+} (70°C)

	Current density, mA/cm^2	3.3	6.7	13.3	20.0	26.7
[Ni^{2+}],0.00mol/l	$Q_{Ce(4+)}$, mM/cm^2*hr	0.114	0.234	0.384	0.330	0.300
[Ni^{2+}],0.05mol/l	$Q_{Ce(4+)}$, mM/cm^2*hr	0.126	0.240	0.390	0.372	0.342

Table XIV Effects of Cr^{3+} on Regeneration Rates of Ce^{4+} (25°C)

	Current density, mA/cm^2	3.3	6.7	13.3	20.0	26.7
[Cr^{3+}],0.00mol/l	$Q_{Ce(4+)}$, mM/cm^2*hr	0.120	0.228	0.384	0.330	0.306
[Cr^{3+}],0.02mol/l	$Q_{Ce(4+)}$, mM/cm^2*hr	0.060	0.090	0.120	0.117	0.108

Table XV Effects of Cr^{3+} on Regeneration Rates of Ce^{4+} (70°C)

	Current density, mA/cm^2	3.3	6.7	13.3	20.0	26.7
[Cr^{3+}],0.00mol/l	$Q_{Ce(4+)}$, mM/cm^2*hr	0.120	0.228	0.384	0.330	0.306
[Cr^{3+}],0.02mol/l	$Q_{Ce(4+)}$, mM/cm^2*hr	0.072	0.120	0.360	0.552	0.474

4.3 Single cell Regenerator and its performance

Based on those results obtained in feasibility investigation, different types of single cell regenerator were designed and tested. According to the results of regeneration rate obtained in preliminary experiments, requirements to structure materials and operation safety, a tube-shaped regenerator was chosen. Polyethylene was used as the structure material and its reduction feature to Ce^{4+} is showed in Table XVI. The self-reduction feature of Ce^{4+} is showed in Table XVII. The titanium plated with platinum and platinum wire were used as the anode and cathode respectively. The single unit of the regenerator is tube-shaped object of ¦µ80 ¡Á 200 mm. The single anode area is about 900cm^2 . The regenerator will be composed with nine units as showed in Fig.1, so the total anode area will be 8100cm^2. A pump is used for recycle and convection. With this regenerator, following performance tests were conducted.

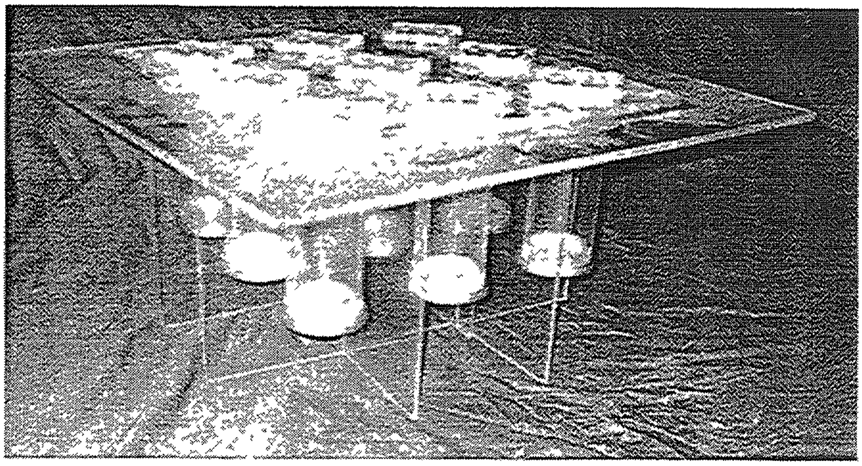


FIG. 1. Appearance of the regenerator.

4.3.1 Effects of Temperature on Regeneration Rates

When concentrations of Ce^{3+} and HNO_3 are 0.20 mol/ and 2 mol/l respectively and the anode current density was maintained at 12.5 mA/cm^2, the experimental results (see Fig.2) show that temperature is a sensitive factor to the regeneration rates of Ce^{4+} and is similar with that of feasibility study. To consider the structure materials of the regeneration cell and the operation safety, lower temperature (about 40°C ~ 50°C) will be recommended.

4.3.2 Effects of Concentration of Ce^{3+} on Regeneration Rates

When the regeneration temperature was 30°C, anode current density remained at 12.5 mA/cm^2, the experimental results (see Fig.3) show that the concentration of Ce^{3+} in the decontamination solution has obvious effect on the regeneration rate of

Table XVI Reduction Feature of Polyethylene to Ce^{4+}

Duration, hr	0.5	1.5	4.0	7.5	12.5	24
Ce^{3+},mMol/l	3.47	4.45	5.65	7.09	7.54	8.33

* [Ce^{4+}]: 0.2mol/l, [HNO_3]: 2mol/l, T: 80°C

Table XVII Ce^{4+} Self-reduction Feature in HNO_3 Solution

Duration, hr	0.5	1.5	4.0	7.5	12.5	24
Ce^{3+}, mmol/l	1.00	3.97	4.07	4.46	4.46	4.96

* [Ce^{4+}] : 0.2mol/l, [HNO_3]: 2mol/l, T: 80°C

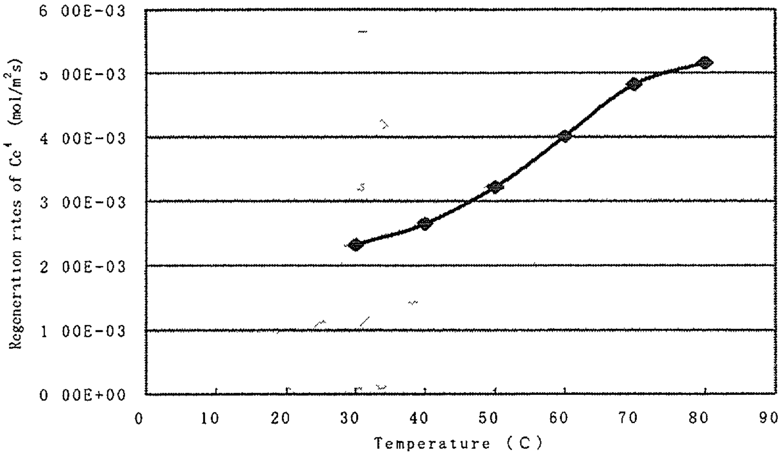


FIG 2 Effects of temperature

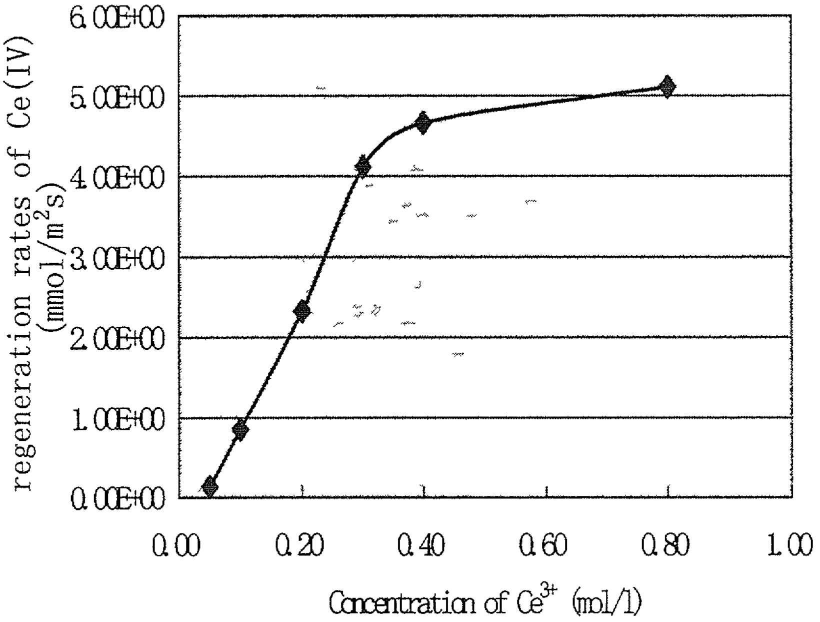


FIG 3 Effects of concentration of Ce(III)

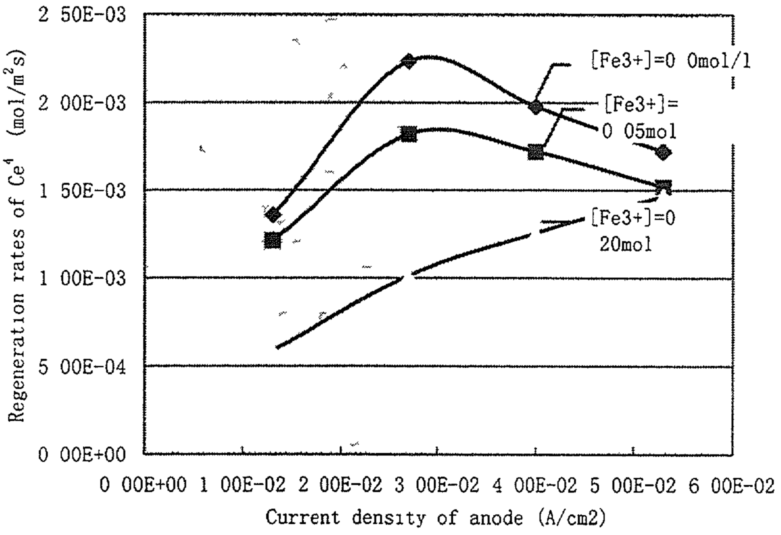


FIG 4 Effects of concentration of Fe^{3+} ion on regeneration rate of Ce^{4+}

Ce^{4+}, when the current density is constant and the concentration of Ce^{3+} is lower than 0.4 mol/l. When concentration of Ce^{3+} is higher than 0.4 mol/l, increase of the regeneration rates with concentration of Ce^{3+} would become much gentler. We would like to choose the concentration of Ce^{3+} in decontamination solution within the range of 0.4 to 0.6 mol/l. So that, higher regeneration rate could be obtained.

4.3.3 Effects of Concentration of Fe^{3+} on Regeneration Rates

As mentioned above, owing to dissolving stainless steel, the concentration of Fe^{3+} in the decontamination solution will increase with progress of decontamination process. Fe^{3+}could be reduced into Fe^{2+} on the cathode of regenerator. Meantime, Fe^{2+} could react with Ce^{4+} and reduce it into Ce^{3+}, so that, we could not get enough Ce^{4+} by regenerator.

When the concentrations of Ce^{3+} and HNO_3 were 0.2 mol/l and 2 mol/l respectively, the experimental results (see Fig.4) show that when current density of anode is sufficient high, for example higher than 5 A/dm^2, existence of Fe^{3+} is no obvious effects on regeneration rates. The most serious effect seems appearance around 2.5 A/dm^2. General speaking, the regeneration rates will not reduce sharply with existence of Fe^{3+}, if the concentration of Fe^{3+} is not higher than 0.2 mol/l.

4.4 Corrosion Rates of Regenerated Ce^{4+} to Stainless Steel

In order to get knowledge about the behaviors of Ce^{4+} regenerated by the regenerator, experiments on corrosion rate to stainless steel so called 1Cr18Ni9Ti were performed. This kind of steel is widely used in Chinese nuclear industry. Its chemical composition is as following: C < 0.12, Si <1.00, Mn <2.00, P < 0 035, S <0.030, Ni 8.00~11.00, Cr 17.00~19.00, Ti 5(C%-0. 02) ~ 0.08.

4.4.1 Effects of Temperature on Corrosion Rates of Stainless Steel

When the concentrations of Ce^{4+} and HNO_3 were 0.40 mol/l and 2 mol/l respectively, the temperature of decontamination solution varied from 30℃ to 80℃, the corrosion rates of stainless steel will increase sharply with the rise of temperature (see Fig.5). That means the operation temperature is a sensitive factor to corrosion

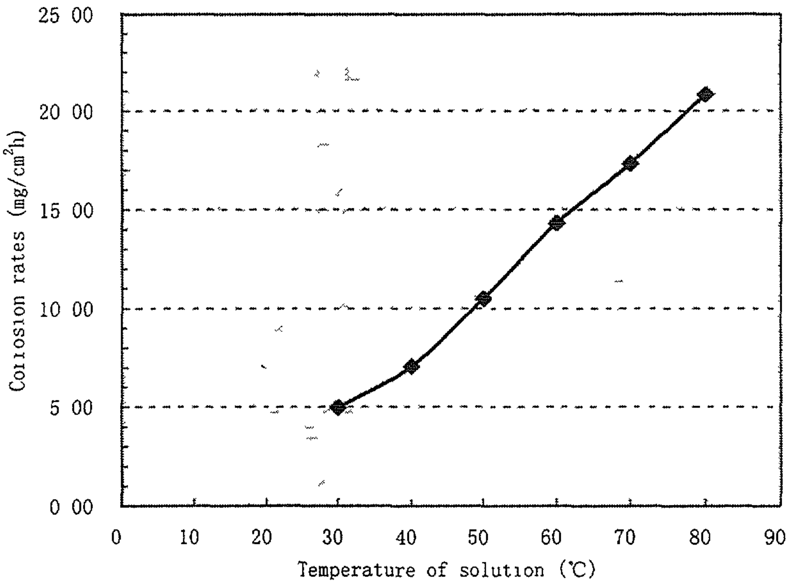


FIG 5 Effects of temperature

rate. We can control the dissolving layer thickness with regulating the operation temperature. But it is difficult to keep it constantly, especially for a long circular loop. We would rather choose lower operation temperature considering the operation safety. In other hand, the corrosion of stainless steel surface will go smoothly and we can get bright surface after decontamination in low concentration of Ce^{4+} at lower operation temperature.

4.4.2 Effects of Concentration of Ce^{4+} on Corrosion Rates of Stainless Steel

The concentration of Ce^{4+} is the main force to dissolve the stainless steel. The experiment results (see Fig.6) show that when the concentration of HNO_3 is 2 mol/l and the temperature is 80°C, the corrosion rate rises rapidly with increase of the concentration of Ce^{4+} at the same operation temperature and it looks like a flat when the concentration of Ce^{4+} is higher than 0.4 mol/l. That implies us to choose concentration of Ce^{4+} as high as possible according to Ce^{4+} regeneration rate and economy balance to control the corrosion rate of metal. Considering our conditions, 0.2 ~0.4 mol/l seems better.

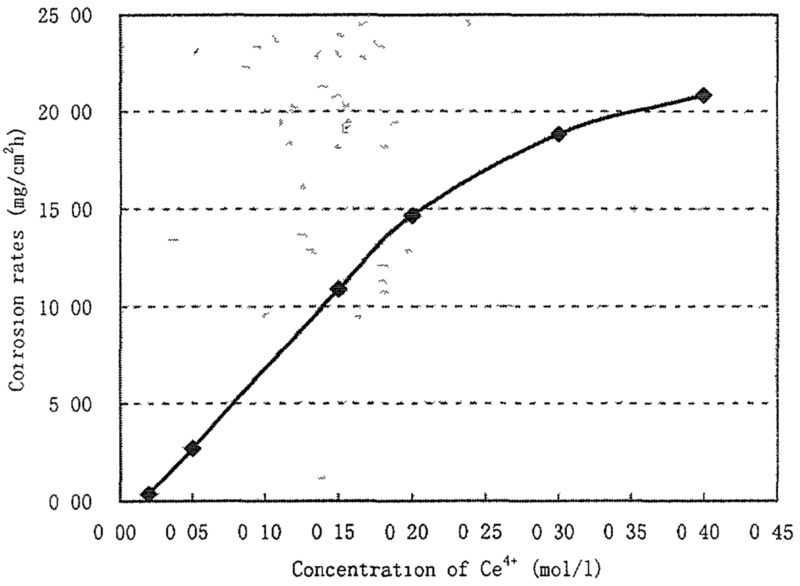


FIG 6 Effects of concentration of Ce^{4+}

4.4.3 Effects of Operation Duration on Corrosion Rates of Stainless Steel

If the concentration of Ce^{4+} could be maintained constantly during decontamination operation, the corrosion rate would be no obvious change But for decontamination of long loop, Ce^{4+} regeneration rate could not meet the requisite amount consumed by metal corrosion. With the operation duration extension, the corrosion rate should become lower and lower. These experimental results will reveal the effects of operation duration when Ce^{4+} was maintained at higher enough concentration. The results (see Fig.7) show that when the initial concentration of Ce^{4+} is 0.40 mol/l, Concentration of HNO_3 is 2 mol/l and temperature is at 30°C, there is no significant effect on corrosion rate, if the Ce^{4+} regeneration rate is higher than 95% of the consuming amounts of Ce^{4+}. That means, can we only use powerful Ce^{4+} regenerator to perform the decontamination job for long loop of metal with lesser volume of radioactive liquid waste to be produced.

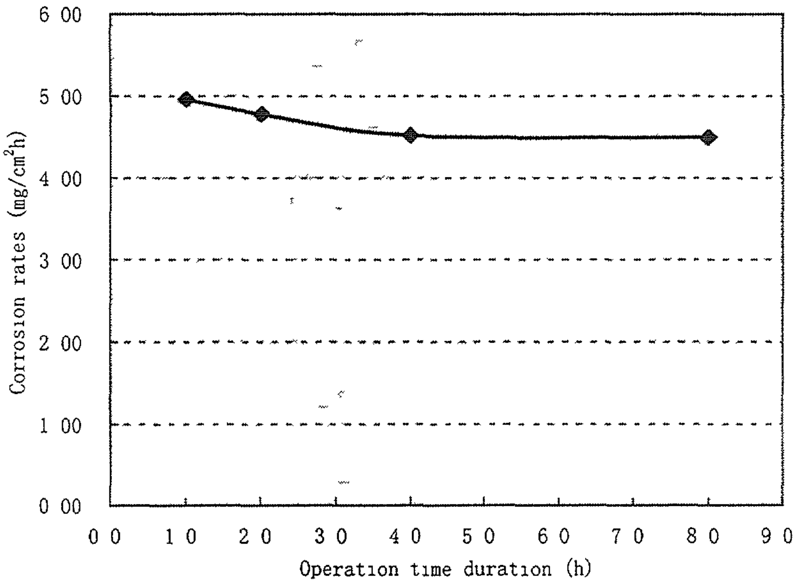


FIG. 7 Effects of time

4.4.4 Effects of Concentration of Nitric Acid on Corrosion Rates of Stainless Steel

Acidity of the decontamination solution is a very important factor, and we hope to operate the decontamination process at lower acidity. The experimental results show that when the concentration of Ce^{4+} is 0.2 mol/l at 30°C, good DFs could be obtained, if the acidity is higher than 2 mol/l of nitric acid (see Fig.8).

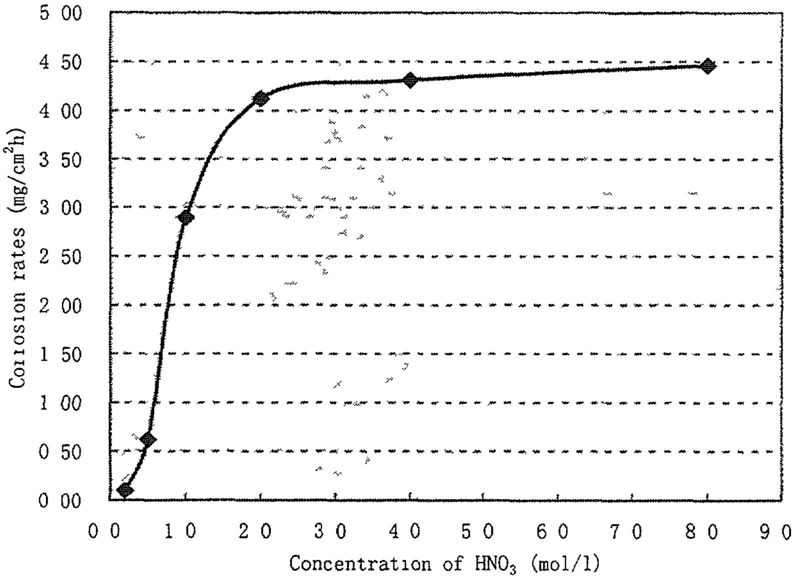


FIG 8. Effects of concentration of HMO3

4.4.5 Corrosion Rates of Stainless Steel in HNO_3 Solution of 2 mol/l

As mentioned above, the highest corrosion rate will be occurred, if the acidity of the decontamination solution is higher than 2 mol/l of nitric acid These experimental results show that lone nitric acid could not raise the corrosion rate, even at 30°C (see Fig.9). That implies that it works as a solvent mainly to remove the oxidation products from the surface of metal and to make new metal surface expose to the decontamination solution, so that, the reaction speed is picked up. But, from Fig.8, we should say that the 2 mol/l of nitric acid is the lowest acidity for our experimental conditions.

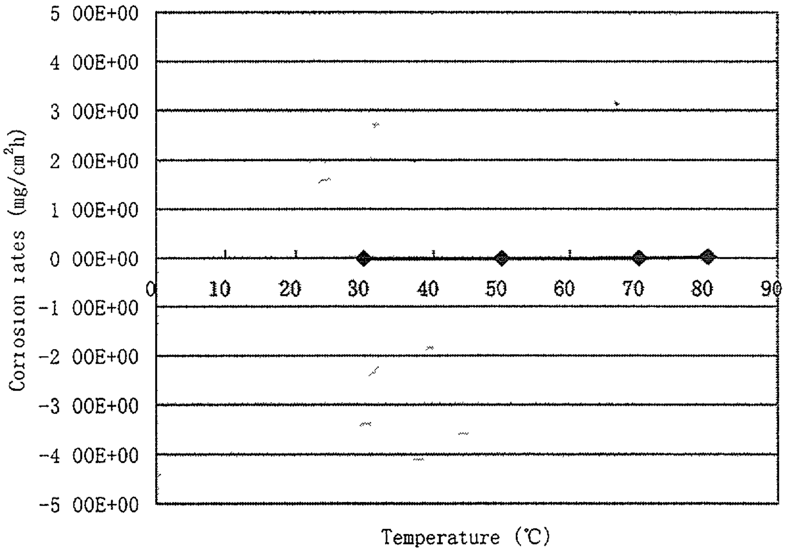


FIG 9 Corrosion rates of stainless steel in HMO3 of 2mol/l

4.4.6 Effects of other factors

One of the other factors, which might seriously affect the corrosion rate of stainless steel in addition to those items mentioned above, may be the state of sample's surface. This is a complicated case, because there are various types of substances, besides contaminants adhered to the surface of stainless steel equipment, their compositions and adhesion varies with the operation conditions. In our experiments, it is difficult to simulate those surface states. To solve those problems, demonstrative tests should be performed with different samples from different nuclear facilities. That means we need experiences But we think that after adjusting the concentration of Ce^{4+} and nitric acid slightly according to real condition, this decontamination process will be working. .

4.5 Treatment of Liquid Waste

Liquid waste coming from this decontamination process should be treated with reducer or electrolysis to return Ce^{4+} into Ce^{3+}, so that, it can safely be stored in a common storage tank, then further conditioned and disposed as normal waste. Our results show that the Ce^{4+} can be reduced into Ce^{3+} immediately with the single cell regenerator, if the electrode will be inverted.

5 CONCLUSIONS

The nitric acid solution containing Ce^{4+} is an effective decontamination solution. This decontamination solution can be regenerated with single compartment regenerator by electrolysis and then recycled or reused for circular loop clean up The special designed single cell regenerator is a tube-shaped object for each unit

The titanium plated with platinum and platinum wire are structural materials for the anode and cathode respectively. Surface area of anode is about 900 cm^2 per unit. The whole regenerator is consisted with nine units. Its maximum regeneration capacity is about Ce^{4+} of 80 mmol/min, when total concentration of cerium is higher than 0.4 mol/l, concentration of nitric acid is around 2 mol/l and the regeneration temperature is within 40°C ~ 50°C.

The corrosion rate of stainless steel in the nitric acid solution containing Ce^{4+} is mainly affected by the concentration of Ce^{4+} and operation temperature, but the other factors should also be considered during parameter selection of decontamination process. This decontamination process could proceed successfully on the basis of our recommended conditions. The basic requirements for this decontamination process are as follows:

- Concentration of Ce (IV) is higher than 0.2 mol/l
- Total concentration of cerium (III+IV) is higher than 0.4 mol/l
- Concentration of nitric acid is higher than 2 mol/l
- Operation temperature is within 25°C ~ 40°C and the regeneration temperature is within 40°C ~ 50°C
- Ce (IV) regeneration rate should meet the consumption rate almost
- Existing iron oxide and organic production must be removed before using this decontamination process
- The liquid waste from decontamination process can safely be stored in a common storage tank after reduction of Ce^{4+} into Ce^{3+}

Further works

A demonstration decontamination should be performed with this decontamination process to verify its performance in the coming year.

REFERENCES

1. Harmon, H. D., "Dissolution of PuO_2 with cerium(IV) and fluoride promoters", in DP – 1371, 1975
2. Partridge, J.A. et al "Decontamination of TRU contaminated metals", in HEPL – TC – 1503, 1979
3. Barry, L. A., "Development of a chemical process using nitric acid – cerium(IV) for decontamination of high level waste canisters", in PNL – 6576, 1988
4. Fujita, R. et al, "Redox decontamination technique development (1) Selection for dissolution and regenerative conditions", pp339 – 349 in Journal of Nuclear Science and Technology, 26(3), 1989
5. Fujita, R. et al, "Redox decontamination technique development (2) Redox decontamination system using pilot plant", pp449 – 458 in Journal of Nuclear Science and Technology, 26(4), 1989
6. Ishibe,T. et al "Redox decontamination technique development using sulfuric acid", pp421 in Proceedings of the 1989 Joint international waste management conference, New York, 1989
7. Suwa, T., et al "Development of chemical decontamination process with sulfuric acid – cerium (IV) for decommissioning, Single step process to dissolve chromium-rich oxides", pp622-632 in Journal of Nuclear Science and Technology, 23(7), 1986
8. Suwa, T., et al "Development of chemical decontamination process with sulfuric acid – cerium (IV) for decommissioning, System decontamination process with electrolytic regeneration of Ce^{4+} from Ce^{3+}", pp574-585 in Journal of Nuclear Science and Technology, 25(7), 1988

FOAM DECONTAMINATION OF LARGE NUCLEAR COMPONENTS BEFORE DISMANTLING

J.R. COSTES, C. SAHUT
Commissariat á l'Energie Atomique,
Rhone Valley Research Center,
Bagnos-sur-Cèze Cedex,
France

Abstract

Following some simple theoretical considerations, the authors show that foam compositions can be advantageously circulated them for a few hours in components requiring decontamination before dismantling. The technique is illustrated on six large ferritic steel valves, then on austenitic steel heat exchangers for which the Ce(III)/Ce(IV) redox pair was used to dissolve the chromium; Ce(III) was reoxidized by ozone injection into the foam vector gas. Biodegradable surfactants are used in the process; tests have shown that the foaming power disappears after a few days, provided the final radioactive liquid waste is adjusted to neutral pH, allowing subsequent coprecipitation of concentration treatment.

INTRODUCTION

Historically, decontamination was an early concern in the development of nuclear power. Manual processes were long used, mainly wiping, water or steam spraying, sandblasting, etc. Less aggressive decontamination processes were subsequently developed for maintenance of nuclear power reactors, using circulating fluids containing mild chemicals; examples include CANDECON, LOMI and EMMAC. The objective is to divide the operational dose by ten by dissolving the surface layer of complex oxides, and with it most of the contamination; the metal itself should remain intact.

For decommissioning purposes, decontamination is intended primarily to reduce the occupational dose (i.e. *in situ* decontamination) and to allow decategorization of nuclear waste (by decontamination before or after cutting). The final cost of waste material varies to a considerable extent according to its residual activity and applicable disposal restrictions. Possible disposal options (by order of decreasing cost) include: geological disposal, surface disposal, very low-level waste disposal, and recycling in the nuclear domain.

In order to reach these objectives, the decontamination factor must be sufficiently high — better than 100 is a reasonable target. This implies removal not only of all the oxides liable to trap contaminants but also of a layer of the substrate itself; the radionuclides tend to collect in the intergranular regions, together with other impurities accumulated during the growth of the metal grains.

These enhanced objectives related to decommissioning have incited innovative developments in the last fifteen years, with potential applications to various USDOE sites, Chernobyl, Greifswald, Windscale, as well as to UP1 (Marcoule) and other French decommissioning projects.

The innovative aspect of this work involves the use of a foam recirculating system (COMODIN) to decontaminate large components. Biological elimination of the surfactants is also discussed as a means of allowing suitable liquid waste treatment.

BACKGROUND AND RESEARCH OBJECTIVES

Few techniques are available for decontaminating large internally contaminated metallic components with complex shapes Spraying does not reach all internal surfaces evenly due to preferential flow patterns Immersion systems are impracticable because of the excessive reactant volume necessary and because the reactants are ineffective on large volumes due to boundary layer phenomena Mechanical methods are inoperative, as they cannot reach all the internal surfaces, and recovery of the abrasion residue would be difficult In contrast, foam application provides a satisfactory solution to all these problems

A major advantage of the foam application process is that it uses only small quantities of liquid, and thus significantly reduces the secondary waste volume (ten times less than with standard decontamination methods such as recirculation of liquid in the component) Moreover, foams are capable of penetrating into all the interstitial gaps in the component, effectively decontaminating all the exposed surfaces The effectiveness of the process is further enhanced by the dynamic mobility of the foam and by continuous regeneration on the component walls, thereby eliminating common boundary layer problems Finally, foam recirculation and continuous filtration of the parent solution allow the treatment to be maintained until decontamination is complete

After a brief study of foam theory, we undertook to apply foams through recirculation in large-scale components (COMODIN) The foam carries strong acid and alkaline reagents to ensure thorough stripping of the contaminated surface The innovative character of the process concerns three aspects

- indefinite recirculation of the foam in components with complex geometry,
- the addition of strong reagents to liquids that are then converted to foam,
- the use of biodegradable surfactants that are self-eliminating to allow subsequent processing of the final radioactive liquid waste

TECHNICAL APPROACH

Foam Stability

One of the most relevant characteristics of a foam is its limited and measurable lifetime Foam stability depends on many factors, including the following fluid viscosity, surface viscosity (which retards draining and film distortion), Marangoni effect (which tends to restore the surfactant distribution equilibrium, preventing the film from breaking), and repulsion of the double electric layer (which maintains the integrity of the lamella)

Although progress has been made in identifying and determining the phenomena involved, foam stability is still not completely understood Three sources of instability are considered here Ostwald ripening, coalescence and draining

Ostwald ripening Small bubbles tend to dissolve while larger ones grow in size by gas diffusion through the continuous phase Ostwald ripening can be remarkably fast, and is considered by some authors to be one of the most destabilizing processes in foams

Coalescence The lamellae burst between foam bubbles leading to coalescence Destabilization of the foam bed thus results in a diminishing film surface area as the number of bubbles decreases and their size increases Coalescence occurs preferentially on contact with solid surfaces, and results in regular release of liquid, thereby improving the decontamination efficiency

Drainage The liquid phase drains under the effects of gravity and of the pressure difference between the flat and curved portions of the film (the pressure in the curved zones, i e the plateau borders contiguous with several bubbles, is always lower than in the flat regions, causing liquid to flow from the films toward the plateau borders)

There is some confusion in the use of these terms, and some authors tend to refer to all three phenomena under the general term of "drainage" "Liquid streaming" will be used in the remainder of this report

Recirculating Foam Decontamination Principles

The foam used consists of a gas, generally air, dispersed in a liquid in proportions such that the mixture density more closely approximates that of a gas than a liquid Suitable surfactants are added to lower the surface tension of the liquid containing chemical decontaminants, and thus facilitate the formation of a foam

Recirculation consists in supplying the component with foam decontaminants, foam flowing out from the top of the component is broken, reformed and recycled back into the unit for periods of up to several hours

The foam is naturally destroyed However, the working life of the foam must be long enough to fill the entire component volume and flow out with sufficient moisture content to ensure good decontamination

Foam Working Life

A test vessel with a volume V is initially filled with foam that is as representative as possible, and the rise in the liquid level L due to coalescence is observed Experimental observations have shown that

$$L = L_0 (1 - e^{kt}) \qquad (1)$$

where t is the time (refer to **Figure 1**) and L_0 the liquid quantity recovered after an infinite time (in fact, the quantity of liquid present in the foam when sampled)

Generally the foam does not break immediately, and fills the entire volume V throughout the observation period This was the case in these experiments as long as the bulk factor ($f = V/L_0$) did not exceed 40

This may also be written $L' = L_0 - L = L_0 \cdot e^{-kt}$ (where L' is the residual liquid trapped in the foam) This formula was proposed by Bikerman[1], other similar formulas are presented by Doufare[2]

Figure 2 shows the function $1 - L/L_0$ versus time plotted in semilogarithmic coordinates If Eqn (1) is verified, the curves should be straight lines, in fact, the actual plot deviates slightly from this simulation

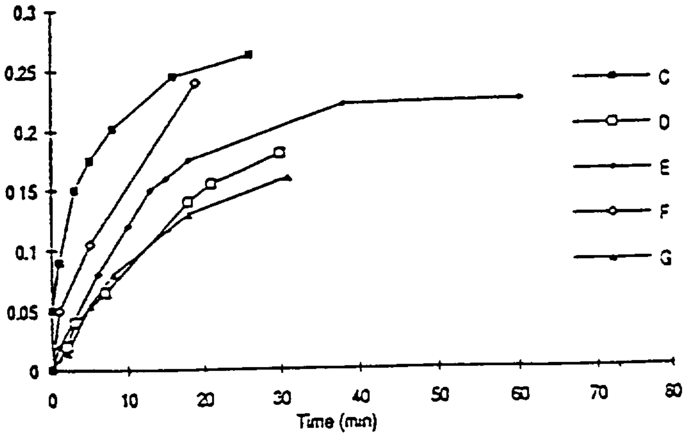


Figure 1 Rise in liquid level due to coalescence

The term "half-life" ($t_{1/2}$) will be used here to represent the time after which $L = L_0/2$ (a more accurate term might be the "half-liquefaction time") Eqn (1) may then be written as follows

$$\frac{L}{L_0} = 1 - e^{-0\ 693\, t/t_{1/2}}$$

Moreover, if f_0 is the initial bulk factor, then

$$f_0 = \frac{V}{L_0} \qquad f' = \frac{V}{L'} \qquad \frac{f'}{f_0} = e^{-0\ 693\, t/t_{1/2}} \qquad (2)$$

It is easy to identify the measured half-life of each numbered foam composition in **Figure 2**, representing one experiment The test foams included a standard acid composition (06a) with a half-life of 8 minutes, and the same foam with 0 5% polyethylene glycol additive (09), which extended the initial half-life to 14 minutes, after 90 minutes in operation, the half-life was only 12 minutes (07) These foams were sampled during the actual application described below

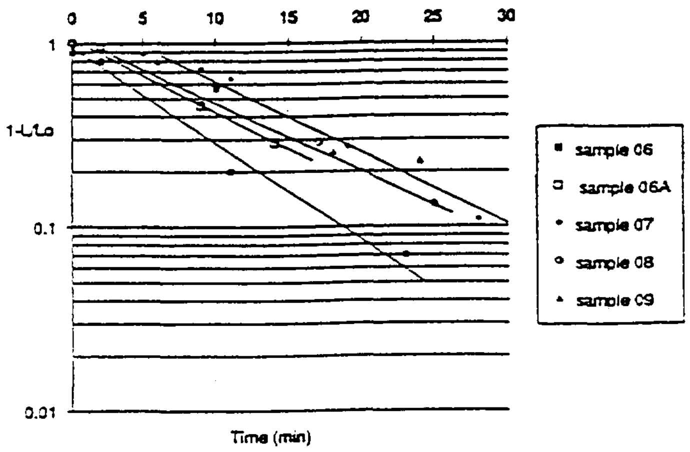


Figure 2. Liquid fraction trapped in the foam

During foam recirculation in the contaminated vessel, foam is injected continuously at a rate R into a vessel with a volume V. For what value of R will it overflow from the top of the vessel with a bulk factor f'? The filling time t_f must be less than the time required for the foam to reach f':

$$t_f < t'$$

where $t_f = V/R$, f becomes R/L' and t' is determined from **Eqn (2)** as follows:

$$t' = \frac{t_{1/2}}{0.693} Ln \frac{f'}{f_0}$$

This is the minimum flow rate R corresponding to the volume V to be filled, for which the foam will overflow with a bulk factor f' that will allow it to be recycled, assuming the foam solidity properties are maintained as long as $f' < 40$.

If f_0 is limited to 7 to ensure satisfactory decontamination of the low points in the vessel, then:

$$t_f < \frac{t_{1/2}}{0.693} Ln \frac{40}{7} \qquad or \qquad t_f < 2.5\, t_{1/2}$$

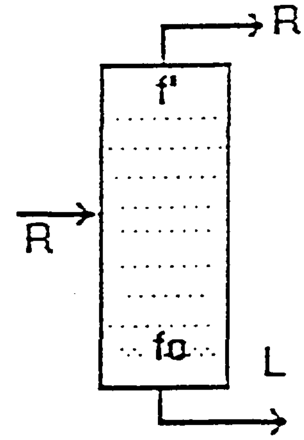
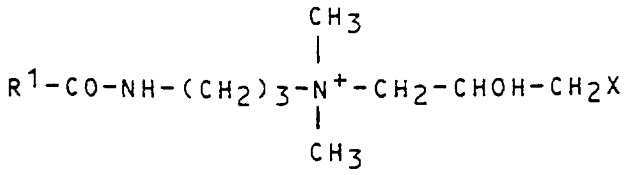


Figure 3. Foam stratification

Foam Formulation Containing Decontaminating Reagents

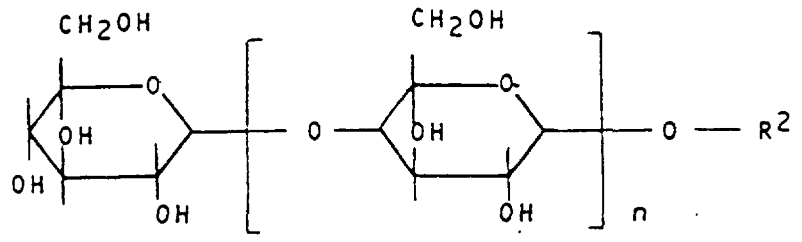
The foam formulation used in this study is based on a CEA patent. The advantage of this foam is that it is compatible with both acid and alkaline environments (up to 5 mol·l^{-1}). The foam comprises two surfactants:

- a sulfobetaine, which is an amphoteric surfactant used to promote film formation and to maintain the relative stability of the two films making up the lamella (electrostatic repulsion):



$$R^1\text{-CO-NH-(CH}_2)_3\text{-}\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle CH_3}{|}}{N^+}}\text{-CH}_2\text{-CHOH-CH}_2X^-$$

- a glycoside alkyl ether, which is a nonionic surfactant used to maintain a high osmotic pressure in the lamella, and thus to reduce the drainage rate:



Alcohol can be used as a destabilizing agent to control the foam moisture content and stability; 2-pentanol is used for alkaline foams, and 4-methyl-2-pentanol for acid foams.

The reagents are prepared in a liquid medium before use. Depending on the formulation, a degreasing, descaling or rinsing effect can be obtained.

ACCOMPLISHMENTS

Application to Large Ferritic Valves with Complex Internal Geometry

A special "COMODIN" dolly was designed on the basis of the preceding theoretical considerations to test the decontamination of a series of large valves with complex internal configurations The valves were made of ordinary low-carbon steel and were taken from the secondary system of a gas-cooled reactor undergoing decommissioning.

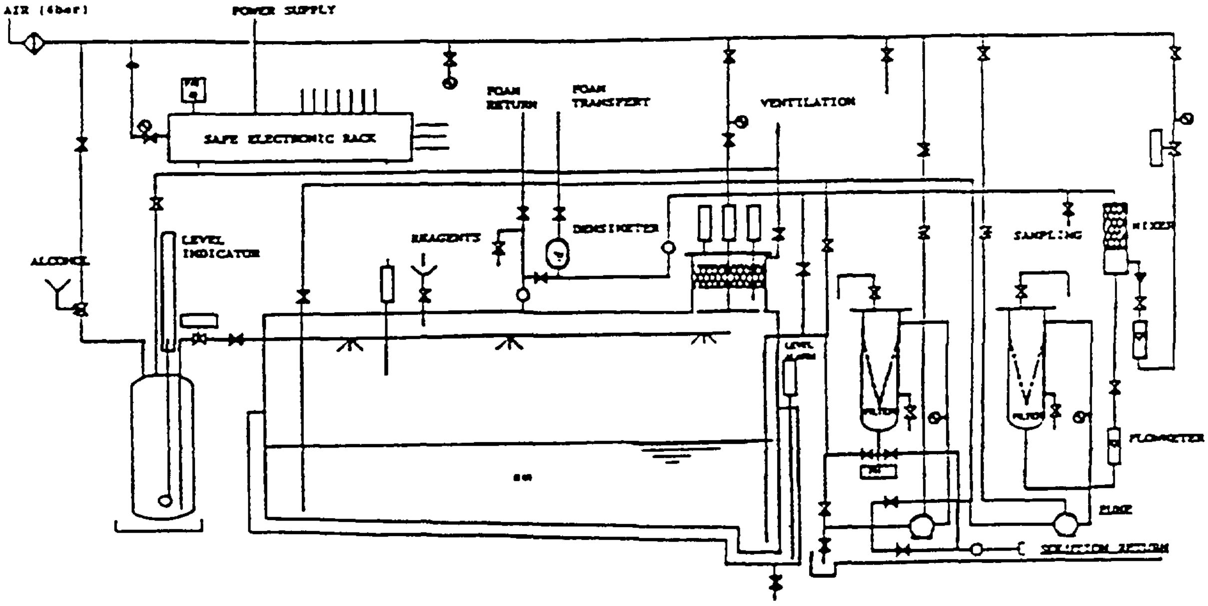


Figure 4. Schematic diagram of decontamination dolly

The COMODIN recirculation unit (**Figure 4**) comprises mainly a tank and hydropneumatic pumps suitable for use with liquids and foams. The system is maintained under slight negative pressure by filtered exhaust blowers. It includes a 4 m^3 rectangular tank inside a safety vessel, a liquid injection pump in the foam generator, and a scavenge pump to recover the liquid overflow from the valve. The pumped fluids are filtered to 20 µm and 100 µm. The foam is produced in high efficiency mixer by injecting compressed air. The foam density is monitored in both the feed and recovery pipes, and the final off-gas stream is monitored. Chemical injection systems may be set up as required. Containment and a negative pressure gradient are provided for the entire unit as standard practice in contaminated environments. The complete dolly is light enough to be transported to the decontamination site. Biodegradable surface-active products are used in the process so the liquid waste stream can be recovered without difficulty by the onsite Liquid Waste Treatment Station, where the radionuclides are removed by coprecipitation.

Procedure

The component is first washed with 3N sodium hydroxide using an unctuous foam with a minimum half-life of 8 minutes and a low bulk factor between 5 and 8. The valve is then decontaminated for 3 to 4 hours with a sulfuric and phosphoric acid mixture well suited to surface etching of ferritic steel, applied as a foam with similar properties. It is then rinsed with a slightly alkaline foam to obtain a relatively neutral final pH on the valve walls, and thus prevent further surface damage.

Operating costs are optimized by using the same reactants twice to decontaminate two identical valves during the same operation. The reactants are mixed to obtain a final pH of 5 to 6 before they are pumped to the liquid waste treatment facility.

Example

Table I summarizes the results obtained with a valve 1.2 m in diameter weighing 5 metric tons, with a unit volume of 3.3 m^3 and a total unit surface area of 24 m^2. The table indicates the total radioactive (mainly ^{60}Co and ^{137}Cs) measured with a surface probe to assess the total contamination and a cotton smear test to evaluate the transferable contamination before and after treatment. After the foam process, most of contamination measurements were below the detection thresholds. The liquid and radioactivity balances are indicated in **Table II**.

Table I. Radioactivity measurements (Bq·cm^{-2}) inside Valve 31

Reference Location	Before Treatment		After Treatment	
	Smear	Probe	Smear	Probe
1	15	12	< 0.2	< 1
2	15	15	< 0.2	< 1
3	< 0.2	< 1	< 0.2	< 1
4	< 0.2	< 1	< 0.2	< 1
5	25	35	< 0.2	< 1
6	6	12	< 0.2	< 1
7	4	8	< 0.2	< 1
8	45	20	< 0.2	< 1
9	65	30	< 0.2	< 1
10	6	< 1	< 0.2	< 1
11	40	25	< 0.2	< 1
12	< 0.2	< 1	< 0.2	< 1
13	50	30	< 0.2	< 1
14	< 0.2	< 1	< 0.2	< 1
15	20	10	< 0.2	< 1
16	< 0.2	< 1	< 0.2	< 1

Table II. Liquid and radioactivity balances

Phase	Liquid volume (liters)	Dissolved activity (MBq)
Alkaline	600	2
Acid	628	4.2
Rinse	605	0.3

An additional 0.6 MBq was retained by the filters, as estimated from dose rate measurements. The average dissolved metal thickness was 10 µm; an average of 15 Bq·cm^{-2} was therefore removed from the two valves. The residual contamination did not exceed 0.1 Bq·g^{-1}, allowing the valves to be melted down for recycling in an approved steel mill. Similar results have been obtained on valves 1.6 m in diameter with a unit volume of 7 m^3. The same dolly was later used to decontaminate a ferritic steel and brass heat exchanger with a surface area of 1000 m^2 and an internal volume of 27 m^3.

Application to Six Large Austenitic Heat Exchangers

Six identical heat exchangers (**Table III**) were contaminated on the shell side by the pool reactor primary cooling fluid. The contamination was estimated by the Radiological Protection Department when the primary system was isolated from the reactor in December 1992: samples were taken from two of the heat exchangers and dose rates were measured around the circumference of the units.

Figure 5 indicates the radioactivity spectrum for heat exchangers 4 and 6 at the time of decontamination. The dose rate was 200 µGy·h^{-1}.

Table III. Contaminated heat exchangers

Unit volume:		
	Tube shell	0.915 m^3
	Head	0.155 m^3
	Base	0.155 m^3
	Total	1.225 m^3
Unit weight:		2700 kg
Contaminated unit surface area:		
	Tubes	214 m^2
	Shell + head and base	18 m^2
	Total	232 m^2

The contaminated heat exchangers were installed three at a time in the basement of the G2 reactor at Marcoule, which has been decommissioned to Stage 2. They were inclined on a cradle (**Figure 6**) to prevent the internal heat exchanger baffles from hindering fluid circulation. Foam was injected at the base of each unit through a safety valve, and flowed out through an orifice at the top for recovery by the COMODIN device. During each decontamination cycle, 50 ml liquid samples were taken from the foam and liquid return lines to measure their dose rates and total Fe concentrations, indicative of the extent of metal dissolution. Between each cycle, the contact dose rates were measured at three points (top, middle and bottom) of the heat exchanger shell.

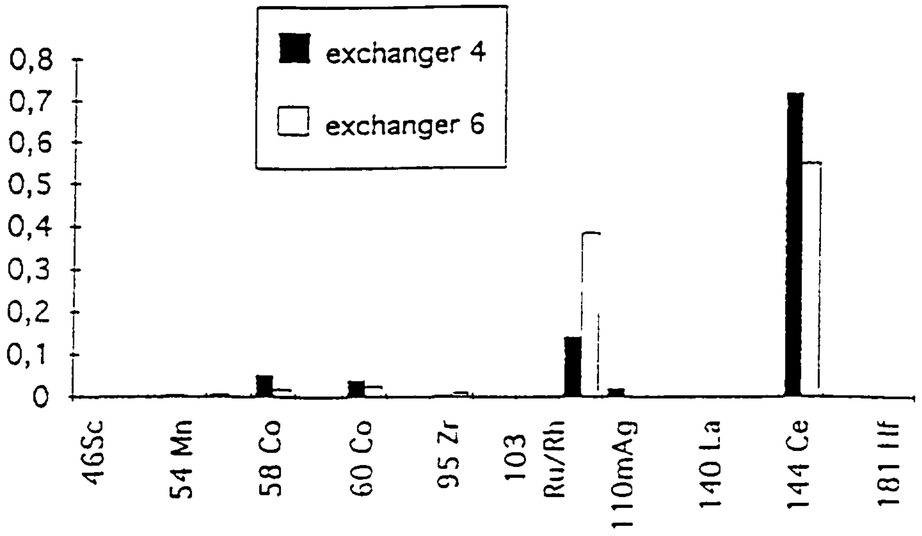


Figure 5. Radioactivity spectra for heat exchangers 4 and 6 prior to decontamination

Decontamination Reactants

Alkaline and acid foams were used in turn, for periods of 4 hours each. The first was a 12% NaOH solution; the second was a mixture of 0.5N sulfuric acid and 2N nitric acid together with $0.04\ \mathrm{mol{\cdot}l^{-1}}$ of $Ce(SO_4)_2$ additive. The alkaline fluid was filtered across 100 µm PALL filter cartridges, and the acid fluid was filtered to 10 µm. The filters were replaced whenever the dose rate reached $1\ \mathrm{mGy{\cdot}h^{-1}}$. The operation was terminated by two foam rinses. The surfactant (0.8 vol%) was a biodegradable mixture of betaine and glycoside covered by a CEA patent.

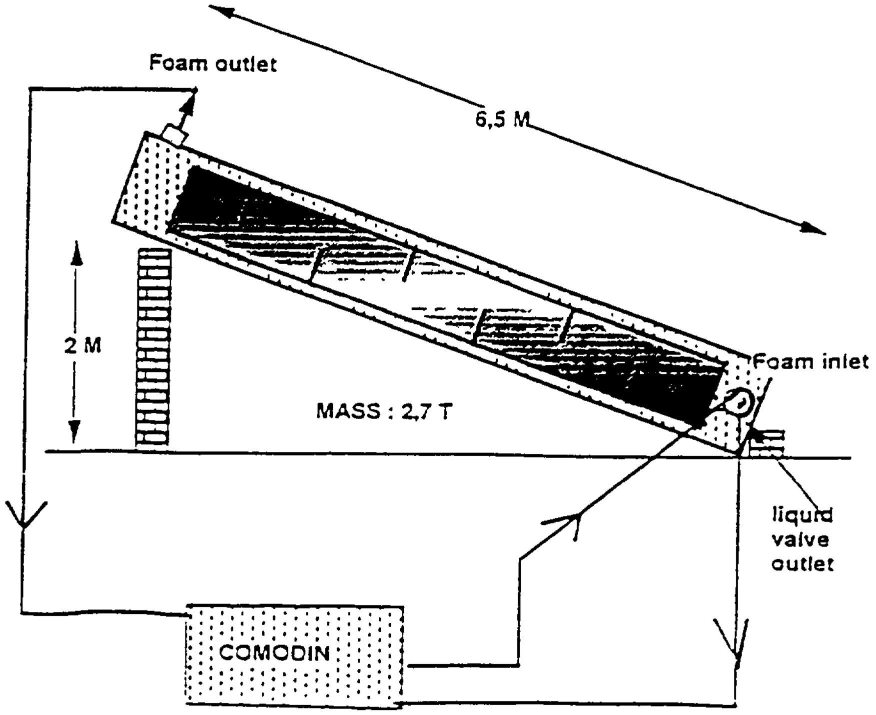


Figure 6. Heat exchanger installed on decontamination cradle

After decontamination, the filtered liquids were pumped into interim storage tanks. The alkaline and acidic liquid wastes were mixed to obtain a neutral fluid (pH 6) and sent via special flow lines to the central liquid waste treatment plant on the site. The salt resulting from this mixture constitutes an effective foam breaking agent.

Decontamination Procedure

The operation was conducted with the working temperature maintained at 20°C

Example 1

This work involved decontamination of five heat exchangers using air-generated foam The Ce(IV) additive was regularly consumed by oxidation of the metal (about 2 g of iron were found per liter of solution) and had to be added continuously, for a total of 16 kg per cycle Decontamination was satisfactory based on the drop in the dose rates (14 $\mu Gy\ h^{-1}$) Only a small quantity (1 m^3) of liquid waste was produced for each heat exchanger

Example 2

Heat exchanger 5 was decontaminated using ozone-enriched oxygen foam (100 g of O_3 per Nm^3 of O_2) with 6 kg of Ce(IV) The reaction progressed some 50% faster than in the preceding test Both acid foam steps provided better decontamination and the dissolved iron quantity was twice as high (4 $g \cdot l^{-1}$) The residual heat exchanger dose rate was lower (< 8 $\mu Gy\ h^{-1}$), while the quantity of liquid waste was comparable to the previous test

The surfactants used to prepare the foam are slowly decomposed on contact with the ozone It could be necessary to add a small quantity of surfactant during the decontamination operation, which may last for several hours However, this drawback is minor in comparison with the advantage of the phenomenon the surfactants are destroyed during interim storage of the liquid waste prior to transfer to the treatment station The foaming power, which could be a nuisance at this stage, is considerably weakened

Activity of the Decontamination Liquid Waste

The liquid waste generated by the decontamination operations were collected, sampled and diluted for analysis by the Marcoule Radiological Protection Department Seven analyses were conducted as part of the waste management procedure to determine the total activity and spectrum for the following waste streams, where the alphabetic suffix A, B or R indicates the type of treatment (acid, basic or rinse) and the number of letters corresponds to the number of the treatment (AA second acid treatment)

• Analysis 1	Heat exchanger 2	basic treatment (2B)
	Heat exchanger 4	basic treatment (4B)
• Analysis 2	Heat exchanger 2	3 acid treatments (2A, 2AA, 2AAA)
	Heat exchanger 4	2 acid treatments (4A, 4AA)
• Analysis 3	Heat exchanger 1	2 acid treatments (1A, 1AA) & basic treatment (1B)
	Heat exchanger 2	rinse (2R)
	Heat exchanger 4	acid treatment (4AAA) & rinse (4R)
	Heat exchanger 6	basic treatment (6B)
• Analysis 4	Heat exchanger 1	2 rinses (1R, 1RR)
	Heat exchanger 3	basic treatment (3B)
	Heat exchanger 6	2 acid treatments (6A, 6AA) & rinse (6R)
• Analysis 5	Heat exchanger 5	acid treatment (5A)
• Analysis 6	Heat exchanger 5	acid treatment (5AA)
• Analysis 7	Heat exchanger 5	basic treatments (5B)

The acidic liquid waste from heat exchanger 3 and the rinse from heat exchanger 5 were not analyzed The liquid waste streams collected and analyzed therefore represent the decontamination of five of the six heat exchangers (1, 2, 4, 5 & 6)

The analysis results are summarized in **Table IV**. The liquid waste activity was calculated by multiplying the activity concentration (determined from the sample) by the liquid waste volume and the sample dilution factor. The total activity of the liquid waste, i.e. of the contamination removed from the heat exchangers, was thus 16.1 GBq. As the analysis results cover only 5 of the 6 heat exchangers decontaminated, the mean contamination removed from each unit may be estimated at 3.22 GBq, and the total contamination was therefore 6 × 3.22 = 19.32 GBq.

Table IV. Table II. Liquid waste analysis results for heat exchanger decontamination

Analysis No.	Liquid waste streams	Liq. waste volume (l)	Sample contamination ($Bq \cdot l^{-1}$)	Sample dilution factor	Total contamination (Bq)
1	2B, 4B	850	5.75×10^5	2	9.78×10^8
2	2A, 2AA, 2AAA, 4A, 4AA	1100	4.85×10^5	5	2.67×10^9
3	2R, 4R, 1A, 1AA, 4AAA, 1B, 6B	1800	6.48×10^4	10	1.17×10^9
4	1R, 1RR, 6R, 6A, 6AA, 3B	1500	5.19×10^4	100	7.79×10^9
5	5A	340	5.24×10^4	100	1.78×10^9
6	5AA	350	1.38×10^4	100	4.83×10^8
7	5B	340	3.63×10^4	100	1.23×10^9
TOTAL		6280	1.83×10^5		1.61×10^{10}

Sample Analysis Results

The specific activity values measured on the samples are indicated in **Table V**. The shell mass was 370 kg, and that of the tube bundle nearly 2330 kg; the total calculated activity in heat exchangers 4, 5 and 6 is also indicated in the table.

Table V. Table III. Heat exchanger analysis results after decontamination

Heat Exchanger		4	5	6
Shell sample specific activity	($Bq \cdot g^{-1}$)	2.2	3.9	4.0
Tube bundle sample specific activity	($Bq \cdot g^{-1}$)	34	9	39
Calculated total shell activity	(Bq)	8.15×10^5	1.45×10^6	1.50×10^6
Calculated total tube bundle activity	(Bq)	7.90×10^7	2.10×10^7	9.10×10^7
Calculated total heat exchanger activity	(Bq)	8.00×10^7	2.25×10^7	9.25×10^7

Decontamination Factor

The decontamination factor obtained by the COMODIN process was calculated from the mean activity removed from the six heat exchangers and from their residual activity:

Residual activity:	0.40 GBq
Removed activity:	19.32 GBq
Calculated initial activity:	19.72 GBq
Decontamination factor:	19.72/0.40 = 49.3

The overall decontamination factor was therefore approximately 50

Heat Exchanger 5

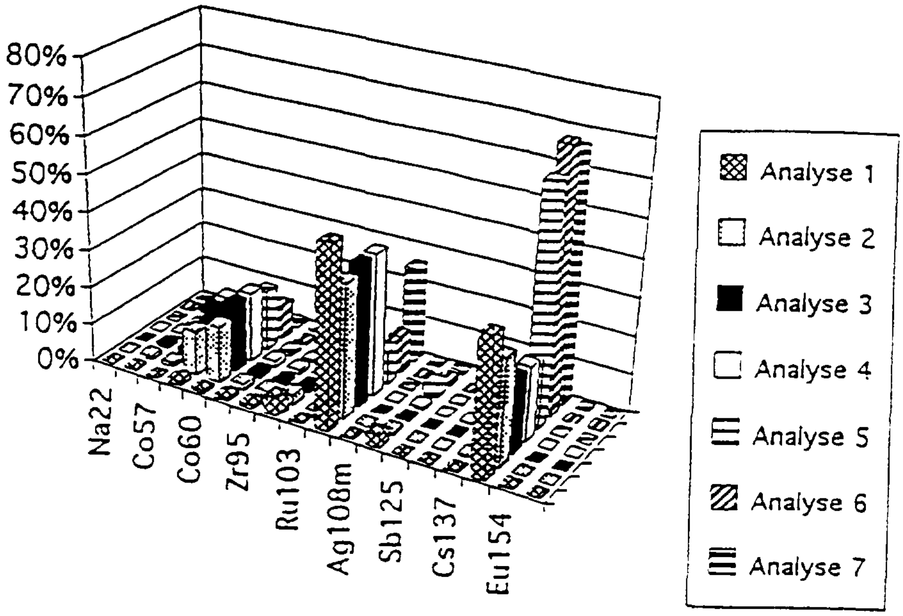


Figure 7. Decontamination liquid waste spectra

Analyses 5, 6 and 7 are of particular interest, as they concern a single heat exchanger, No. 5. The activity removed by the decontamination process amounted to 3.49 GBq and the residual activity was 0.022 GBq; the decontamination factor of nearly 160 was three times higher than the overall factor.

The radioactivity of the tube bundle was 100 times higher than the shell for heat exchanger 4, and 60 times higher for heat exchanger 6, but only 14 time higher for heat exchanger 5. As the shell activity was comparable for all the units, the residual activity of the tube bundle was therefore appreciably lower in heat exchanger 5.

Secondary Liquid Waste Spectrum

The liquid waste spectra are compared in **Figure** 7. The spectra for heat exchanger 5 (analyses 5, 6 and 7) are distinguished by their very high ^{144}Ce content, while the other spectra (for units 1, 2, 4 and 6) are more homogeneous.

Table VI indicates the concentrations of the three principal radionuclides (ruthenium, cerium and cobalt) found in the liquid waste streams. The basic treatment effluents contained significantly greater amounts of ruthenium (26 to 49%) than the acid treatment effluents (9 to 19%); basic treatments are thus apparently more effective for ^{106}Ru decontamination. The opposite appears to be true for ^{60}Co, which is more effectively eliminated by acid treatment. The situation is less clear for ^{144}Ce decontamination, with comparable values for both basic and acid treatments, but with a high degree of residual cerium entrainment in the rinses.

Table VI. Table IV. Ruthenium, cerium and cobalt concentrations in process liquid waste

Treatment	Basic treatments			Acid treatments				
	2B, 4B	5B	6B	5A	5AA	2A, 2AA, 2AAA, 4A, 4AA	6A	6AA
Ruthenium	49%	26%	26%	9%	10%	9%	19%	13%
Cerium	37%	66%	63%	63%	70%	70%	49%	58%
Cobalt	2%	1%	3%	19%	15%	17%	26%	19%

Residual Activity Spectrum

Figure 8 shows the radioactivity spectrum of the samples taken after decontamination prior to melting. The mean spectrum was determined by calculating the average of the mean spectra for the shell and tube bundle, with allowance for the weight differences between them.

The most significant radionuclides were ^{60}Co (30.4%) ^{106}Ru/Rh (17.5%) ^{110m}Ag (32.4%) and ^{144}Ce (8%). Note the high concentration of ^{110m}Ag, which was not predominant in the spectra recorded before decontamination.

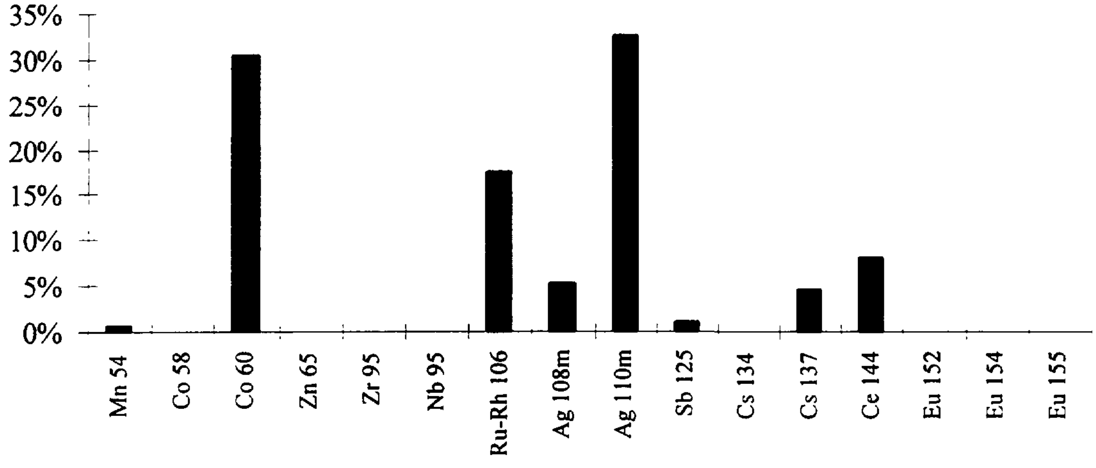


Figure 8. Mean residual activity spectrum

Application Results

In view of the satisfactory results obtained on ferritic steel valves of complicated shapes, and at the request of a pool reactor operator, the CEA's nuclear facilities decommissioning unit (UDIN) submitted six stainless steel heat exchangers to a decontamination and decommissioning treatment consisting of the following operations:

- foam decontamination by the COMODIN process (with ozone-enriched foam for one of the units);
- cutting of each heat exchanger into four sections for dimensional compatibility with the specialized melting facility at Marcoule;
- melting;
- reutilization of the very low-level contaminated steel in the nuclear industry.

Radiological monitoring was conducted throughout the treatment:

- radioactivity assessment by dose rate measurements and application of transfer functions corresponding to the contamination spectrum prior to decontamination;
- quantitative laboratory analysis of the liquid waste generated by the decontamination process;
- assessment of the residual radioactivity after decontamination and before melting on samples taken from the tubes and outer shell of three heat exchangers for laboratory analysis.

The occupational dose rate was 1.2 man-mSv for the entire operation.

The COMODIN Ce(IV) foam decontamination process yielded a mean decontamination factor between 40 and 50, for an initial radioactivity level of about 20 GBq. Ozone-enriched oxygen in the process applied specifically to heat exchanger No. 5 significantly increased the decontamination factor to 160 for that heat exchanger; ozone management raised no major difficulties. Basic treatments proved more effective than acid treatments in eliminating ^{106}Ru. The metal ingots are suitable for recycling, in view of the additional decontamination factor of 3 provided by the melting process itself.

Biodegradability of Surfactants Before Radioactive Liquid Waste Treatment

Low-level liquid waste is generally filtered and treated by precipitation or concentrated by evaporation before the concentrates are conditioned in an inert matrix such as bitumen or cement. A foaming solution cannot be concentrated in an evaporator; even the addition of foam breaking agents does not prevent a high concentration of organic matter. Prior treatment is therefore necessary to reduce or eliminate the foaming power and mineralize the organic matter from the surfactants. However, the very high ionic strength (6M) of these solutions is extremely unfavorable to biological activity.

Principle

Several studies have already shown that microbiological activity persists even under extreme conditions; microorganisms are capable of adapting to a wide range of environmental conditions. We therefore decided to work with wild strains where possible. Decontamination solutions were therefore spread over a soil plot and suitable humidity was maintained to favor natural selection. The objective was to obtain a solution containing a source of carbon, nitrogen, phosphorus, sulfur, sodium, potassium and micronutrients. The physical and chemical conditions (pH, ionic strength, temperature) then had to be adjusted to values compatible with microbial development.

Material and Methods

Decontamination solutions. The solution compounds used for decontamination were provided by the Decontamination Techniques Research Laboratory (DESD/SEP) at Cadarache. An acid solution (A) and a basic solution (B) were prepared; the solution compositions are indicated in **Table VII**. Following a decontamination operation, the two solutions were mixed in equal volume proportions to obtain a solution with 6M ionic strength and a pH of 1.5. As such, the solutions are incompatible with a biodegradation process. We therefore adjusted the pH to 7 using KOH, then added $2\ g \cdot l^{-1}$ of ammonium sulfate (the other required nutrients were already present in the solutions) and diluted them (1/4, then 1/3) to diminish the ionic strength.

Table VII. Foam decontamination solutions

Acid solution			
Compound	Weight (g)	Volume (ml)	Proportions
H_2O	691.58	691.58	-
H_3PO_4 (85%)	353.45	209.14	3.5 moles
HNO_3 (68%)	117.86	83.59	2.5 moles
Oramix (60%)	9.49	8.87	0.8%
Amonyl (50%)	3.44	3.07	0.3%
M4P2	3.00	3.75	0.25%
TOTAL	1178.82	1000.00	-

Basic solution			
Compound	Weight (g)	Volume (ml)	Proportions
H_2O	882	882	-
NaOH (47–50%)	164.89	107.77	2 moles
Oramix	4.20	3.93	0.4%
Amonyl	3.17	2.83	0.3%
M4P2	2.64	3.3	0.25%
TOTAL	1056.90	999.83	-

COD measurement. The Chemical Oxygen Demand (COD) is the quantity of oxygen (in milligrams) consumed by oxidizable matter under the test conditions in a one-liter sample. We determined the solution COD values to provide an indirect assessment of the degradation of the compounds: a lower COD over time corresponds to a smaller quantity of oxidizable organic matter, i.e. surfactants in this case.

TOC measurement. The Total Organic Carbon (TOC) in a one-liter sample is expressed in milligrams. Carbon species are chemically oxidized by sodium persulfate under ultraviolet radiation. The CO_2 generated by the oxidation reaction is observed by a specific infrared detector, and the resulting electrical signal is automatically converted into concentration units. We found a correlation between the solution COD, the TOC and the solution foam: COD = 3.4 TOC.

Metal analysis. The metal concentrations were determined by atomic absorption flame spectrometry (Perkin Elmer 3110) after acidification to pH < 1.5 with HNO_3. This technique is based on the absorption of photons by atoms when excited by a light source of a specific wavelength.

Microorganisms. The surfactant solutions were spread over a soil plot maintained at a suitable humidity. A soil sample was taken after a few days and stirred for several hours in a saline solution at room temperature. Microscopic observation of the solution revealed abundant, varied and highly mobile flora, although no attempt was made to identify the species. The solution was then used to inoculate the surfactant solutions. The cell concentration in the reactors was determined by dry weight measurements: the culture was centrifuged and rinsed twice, and the supernatant was dried at 100°C until its weight remained constant.

Flasks. The first tests were carried out in 500 ml Erlenmeyer flasks containing 100 ml of solution seeded with 10% mixed bacteria. The flasks were continuously stirred at 150 rpm and maintained at 30°C.

Reactors (Figure 9). Tests were carried out in a stirred reactor under the following conditions:

- Continuous supply of nutrient medium and removal of degraded medium at the same rate
- Reactor volume: 1.1 liter
- Temperature: 30°C
- Solution: A + B neutralized to pH 7 using KOH, + 2 $g{\cdot}l^{-1}$ ammonium sulfate, diluted 3 to 4 times to obtain an ionic strength of 1.5–2M.
- Feed rate: variable from an initial value of 7.3 $ml{\cdot}h^{-1}$ to 14 $ml{\cdot}h^{-1}$ (corresponding to a 3.5-day residence time). The parameter values were gradually increased according to the results obtained.
- Demineralized makeup water to compensate for evaporation.

Another reactor also contained metals at a concentration of 10 ppm (Zn-Cu) (Cr-Ni). The concentrations were increased according to the biodegradation results.

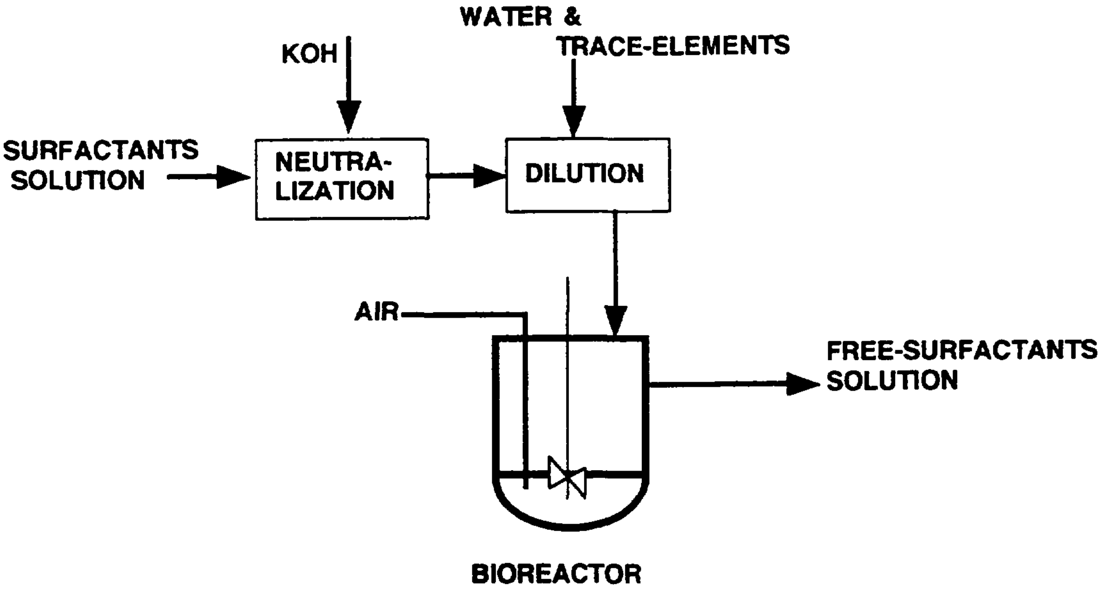


Figure 9. Biodegradation in a continuous reactor: process block diagram

Results

Microorganisms. The microorganisms in the bacterial consortium were not identified. Microscopic observation revealed a highly mobile flora of varying diversity in time.

Biodegradation tests in stirred, aerated flasks. In unseeded control flasks the solution COD diminished in time as the alcohol evaporated from the mixture. This decrease was quantified to determine the actual contribution of the microorganisms to degradation. Control samples were prepared from a 32.5% surfactant solution under the following conditions:

- unseeded, unstirred, pH 1.5
- unseeded, stirred, aerated, pH 1.5
- unseeded, stirred, aerated, pH 7
- seeded, stirred, aerated, pH 7

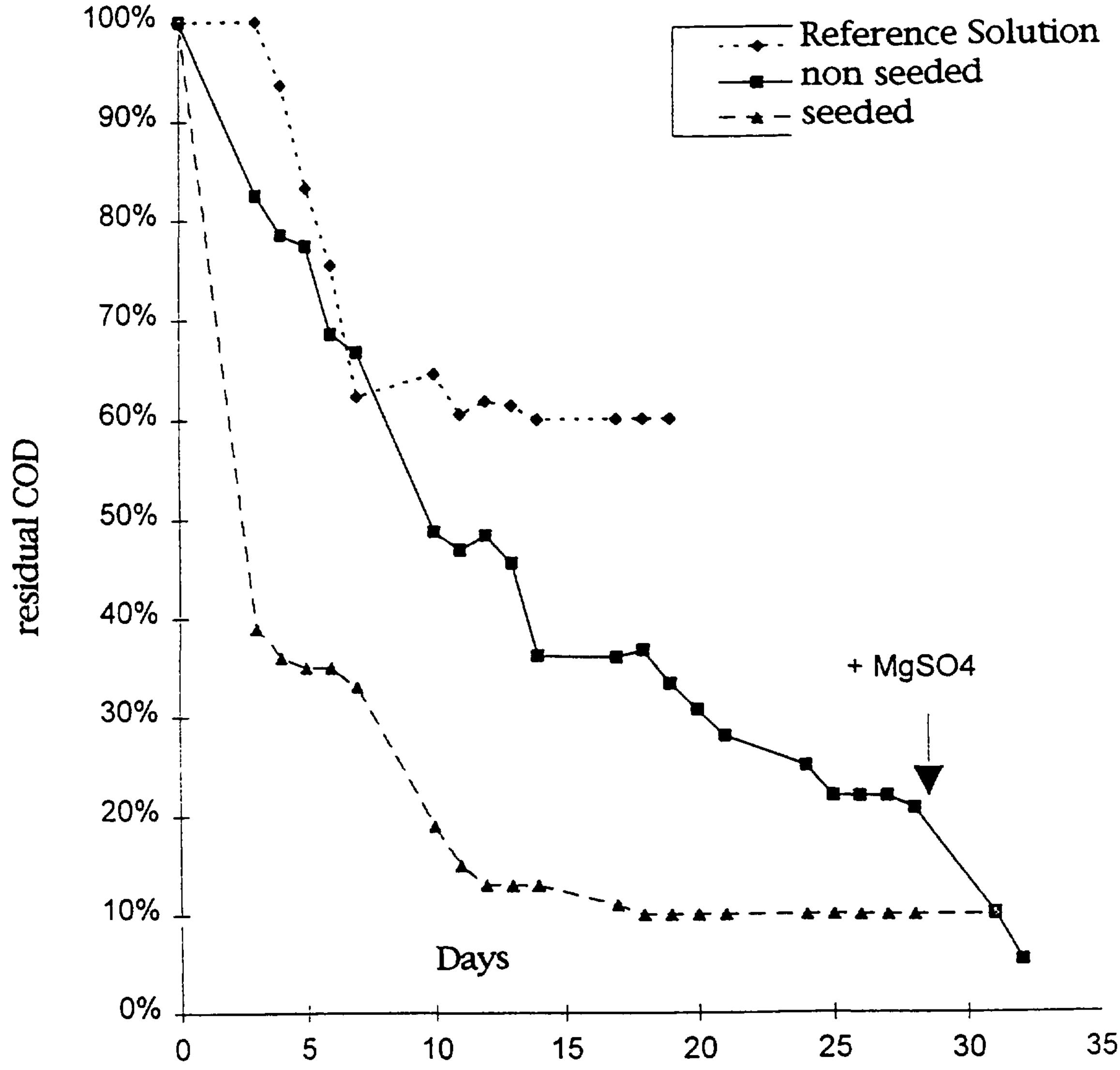


Figure 10. Biodegradation kinetics of surfactant mixtures in stirred, aerated flasks

The results are indicated in Figure 10. The COD of the surfactant mixture at pH 1.5 dropped by about 15% without stirring, and by 35% when aerated. When the mixture was neutralized it was naturally contaminated and the COD diminished by 70% over two weeks. When the same mixture was seeded with the bacterial consortium, the COD decreased by 90% over the same time interval. The biodegradation percentage was improved by adding air to the medium and by more vigorous stirring that favored bacterial development. Full biodegradation was never obtained, however, suggesting a deficiency in one or more elements required for bacterial development. Adding 2 mg·l^{-1} of $MgSO_4$ to the unseeded control sample resulted in 95% biodegradation.

COD-foam relation. It is difficult to quantify the foam generated from a small volume sample, as the height of the foam, its persistence and its consistency must be taken into account. We attempted to correlate the COD and the foam height: no significant foaming seems to occur when the COD is below 600 mg·l^{-1}.

Reactor Tests

Tests were conducted in a reactor continuously supplied for eighteen months, during which the operating conditions evolved according to the results observed.

Without metals. The initial tests began with a 25% mixture and a 5-day residence time in the fermentor, resulting in a 95% reduction in the COD. The surfactant concentration was regularly increased (up to 32.5%) and the residence time diminished (to 3 days). Under these conditions (**Figure 11**), as for the aerated flask tests, the COD diminished by about 85%, exceeding the theoretical value of 64%).

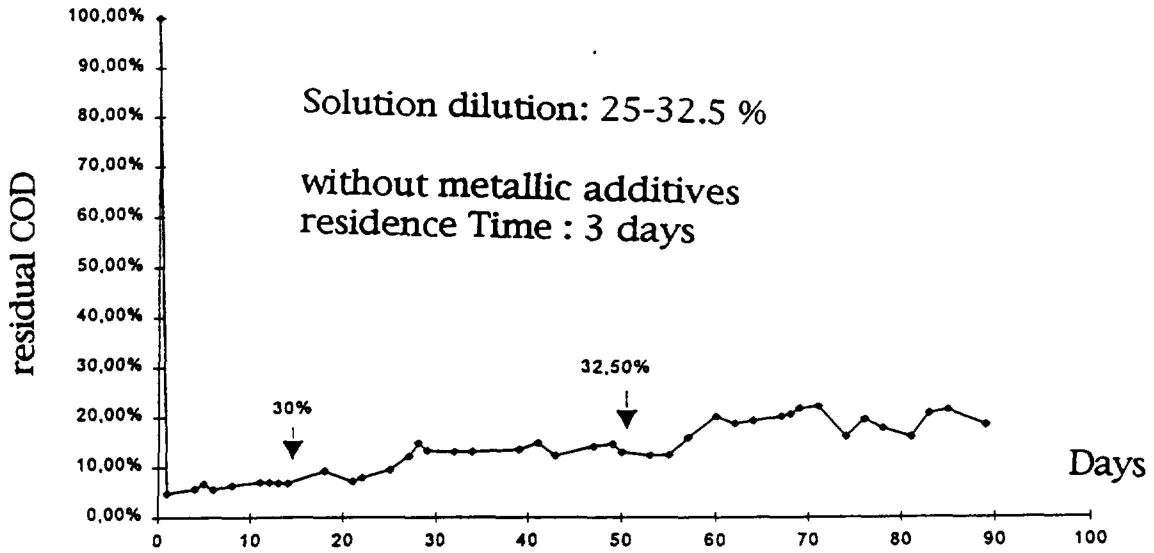


Figure 11. Biodegradation of surfactants in a continuous reactor

With metals. The results obtained were comparable to those observed in the other reactors. The presence of metals at the test concentrations thus appears to have effect on bacterial activity. Determinations after biodegradation on the filter media showed that the metal concentration was constant for copper, zinc and nickel: i.e. no fixation occurred on the biomass. In the case of chromium, however, hydroxides were formed and fixation occurred on the biomass adhering to the reactor walls, or directly on the walls.

Discussion

Using a soil suspension, we selected a bacterial consortium capable of biodegrading the surfactants. The bacterial strains have not yet been identified.

The three surfactants concerned (a natural glucose derivative, a sulfobetaine and an alcohol) were tested separately to determine their biodegradability. The alcohol was quickly and completely degraded, while the other two compounds – particularly the glucose derivative – produced biodegradation residues.

Tests were conducted in aerated media resulted in high biodegradation efficiency, and thus highlights the importance of aeration in sustaining the activity of the microorganisms responsible for biodegradation.

As for the aerated flask tests, the biodegradation test results in a continuous fermentation reactor exceeded the theoretical yield. Satisfactory results were obtained with a solution diluted three times: approximately 80% degradation of the COD was obtained with a 3-day residence time.

It may be necessary to add micronutrients to the surfactant solution to optimize the microbial activity in the reactor and obtain still higher yields; this hypothesis is now being investigated. Even at this stage, however, the reactor outflow solution no longer foams. This is the most important point in the scope of this study.

CONCLUSION

Aqueous phases are used for most wet processes. One possibility is the use liquids flowing at rates for which the Reynolds number exceeds 3000. Strong acids and bases are generally used as reactants, as well as strong oxidation-reduction pairs such as Ce(IV) and Ce(III). Not unexpectedly, these processes generate large quantities of liquid waste, although techniques such as spraying or regenerating the reactant with ion exchangers tend to limit the waste volume.

A more recent alternative (COMODIN process) involves recirculating foam for several hours in the workpiece. This method is suitable for components with complex shapes (e.g. heat exchangers and valves) since the foam is capable of expanding and coalescing in any volume accessible to the contaminants. The most satisfactory foam compositions use biodegradable surfactants and are suitable for use with strong acids and bases as well as a variety of redox agents: Ag(II), Ce(IV), Cr(VI), Co(III), AmO_2(II), MnO_4^{2-}, etc. The redox agents are carefully selected (or paired) to match the contamination. Ce(IV) is highly effective for dissolving chromium oxides on the surface of stainless steel, for example, while Co(III) can effectively remove ^{60}Co from grain boundaries; the same is true of AmO_2(II) for the transuranic nuclides. A further advantage of redox foams is that their action can easily be enhanced by injecting ozone-enriched oxygen into the vector gas: the high oxidation potential reoxidizes the redox agent to the next higher state.

New sequestering molecules (calixarenes, cobalt dicarbollide, etc.) could be used to make foams more selective. Milder reactants, such as borates, are also suitable for decontamination purposes.

Major decommissioning programs already in progress and more are to come. Considering that 30% of the costs involve waste management, new waste decategorization systems such as COMODIN must be developed. They present the additional advantage of allowing operators to work at a greater distance from the irradiating zones without requiring the use of complex robotic techniques.

REFERENCES

1. J.J. Bikerman and J.M. Perri, *Foams: Theory and Industrial Applications*, Reinhold Publishing Corporation (1953).
2. A. Doufare, *Contribution à la mise au point d'une méthodologie nouvelle pour la mesure de la stabilité des mousses liquides*, Ph.D. thesis, University of Pau, France (1987).

DEVELOPMENT OF MELTING FACILITIES AND TECHNIQUES FOR DECONTAMINATION AND RECYCLING OF RADIOACTIVELY CONTAMINATED MATERIAL

W. STEINWARZ
Siempelkamp Nuklear- and Umwelttechnick GmbH & Co.,
Krefeld, Germany

Abstract

One decade after the accident at unit 4 of the Chernobyl nuclear power station a melting plant for radioactively contaminated metallic materials, the so-called SURF facility is being planned and licensed for erection in the direct neighbourhood of the NPP area.

Main goal is the recycling of the material, largely decontaminated by the melting process, by means of manufacturing of casks and containers for waste disposal and of shielding equipment.

The melting plant will be placed as part of the Ukrainian waste handling centre (CPPRO). The technology is based on the long-term experience gained at Siempelkamp's CARLA plant in Krefeld.

In 1995-1997 the licensing conditions were defined, the licensing documents prepared and the formal procedure initiated.

For completion of the recycling technique and to broaden the application fields for the re-usable material a granules production method has been developed and formally qualified. The essential is the substitution of the hematite portion in concrete structures providing an alternative sink for recycling material.

1. INTRODUCTION

Maintenance and decommissioning of nuclear installations will generate increasing quantities of radioactively contaminated and activated metallic residues which have to be disposed off finally. During the last decade melting technology has been developed and commercially established as an adequate safe method for recycling of such materials saving costly storage volume and reducing consumption of raw steel [1].

More than half of the approx. 20,000 Mg of the contaminated metal scrap melted so far worldwide on an industrial scale has been handled by the CARLA plant (central plant for the recycling of low-level radioactive waste) at Siempelkamp/Krefeld (Fig. 1).

The method is based mainly on a separation effect of the radiologically dominant nuclides during the melting process at roughly 1500°C, which leads to a significant transfer of these radionuclides into the process waste such as slag and filter dust, representing only a few percent of the overall mass.

Fig 1 CARLA plant at Siempelkamp's Krefeld location

Thus, the following main advantages of the melting technology can be claimed:

- Substantial reduction of the waste volume compared to other standard handling
- Decontamination of the basic metallic material
- Homogeneous distribution of the residual contamination in the ingots
- Easy classification by precise and reliable radiological measurements by spectroscopy of the melted material qualifying it for the most favourable reuse

The latter allows the recycling of the treated metal to be used as valuable raw material for the manufacture of waste containers, shielding equipment and other products used in the nuclear cycle

Under favourable conditions of very high decontamination factors recycling inside the conventional field can be realized, if the so-called clearance level for unrestricted reuse, defined by the legal authorities and differing from country to country, can be fulfilled.

2. BACKGROUND AND OBJECTIVES OF THE RESEARCH PROJECT

Based on this technology and on the long-term experience gained at the CARLA plant a melting plant for radioactively contaminated metallic materials, the so-called SURF facility (Smelter for the Ukrainian Radwaste Facility) is being planned and licensed to be erected in the neighbourhood of the Chernobyl nuclear power plant as part of the waste handling centre

Main goals are

- manufacturing of casks and containers for storage and final disposal of radioactive waste,
- production of shielding equipment such as plates, beams and cubes of different geometries and sizes to be used for the sarcophagus work at unit 4 and other shielding tasks within the 30 km-zone (e. g. storage facilities).

As first CRP objective elaboration of the basic design and the frame conditions for the licensing procedure has been defined under special consideration of the general requirements in the Chernobyl area, followed by the initiation of the first licensing steps.

For completion of the recycling technique as second CRP objective development of a granulation process for high-alloyed steel scrap has been selected.

3. TECHNICAL APPROACH

3.1 MELTING PLANT AT THE CHERNOBYL SITE

3.1.1 On-site evaluation

In order to provide adequate input data for the SURF plant design and the suitable equipment an on-site evaluation was performed [2]. It showed that radioactively contaminated metallic material is being stored openly at 48 locations within the 30 km exclusion zone. The main part with approx. 60,000 Mg is located in the immediate vicinity of the Chernobyl plant consisting of spare parts such as pipes, vessels and electronic equipment (Fig. 2). In total an overall mass of metal scrap of minimum 100,000 Mg could be estimated, not included the unregistered emergency dumps and the metallic structural materials expected to arise following the plant decommissioning.

The on-site measurements showed furthermore the dominance of Cs 137 and Sr 90 leading to a maximum specific β-/γ-activity of approx. 400 Bq/g as well as the very low portion of α-activity.

3.1.2 Plant concept

According to these results a plant throughput of approximately 10,000 Mg/a was defined with the option to enhance the capacity by modular units.
Main data and the general arrangement of the overall plant are presented in Fig. 3, the process flow with the main procedural steps in Fig. 4.

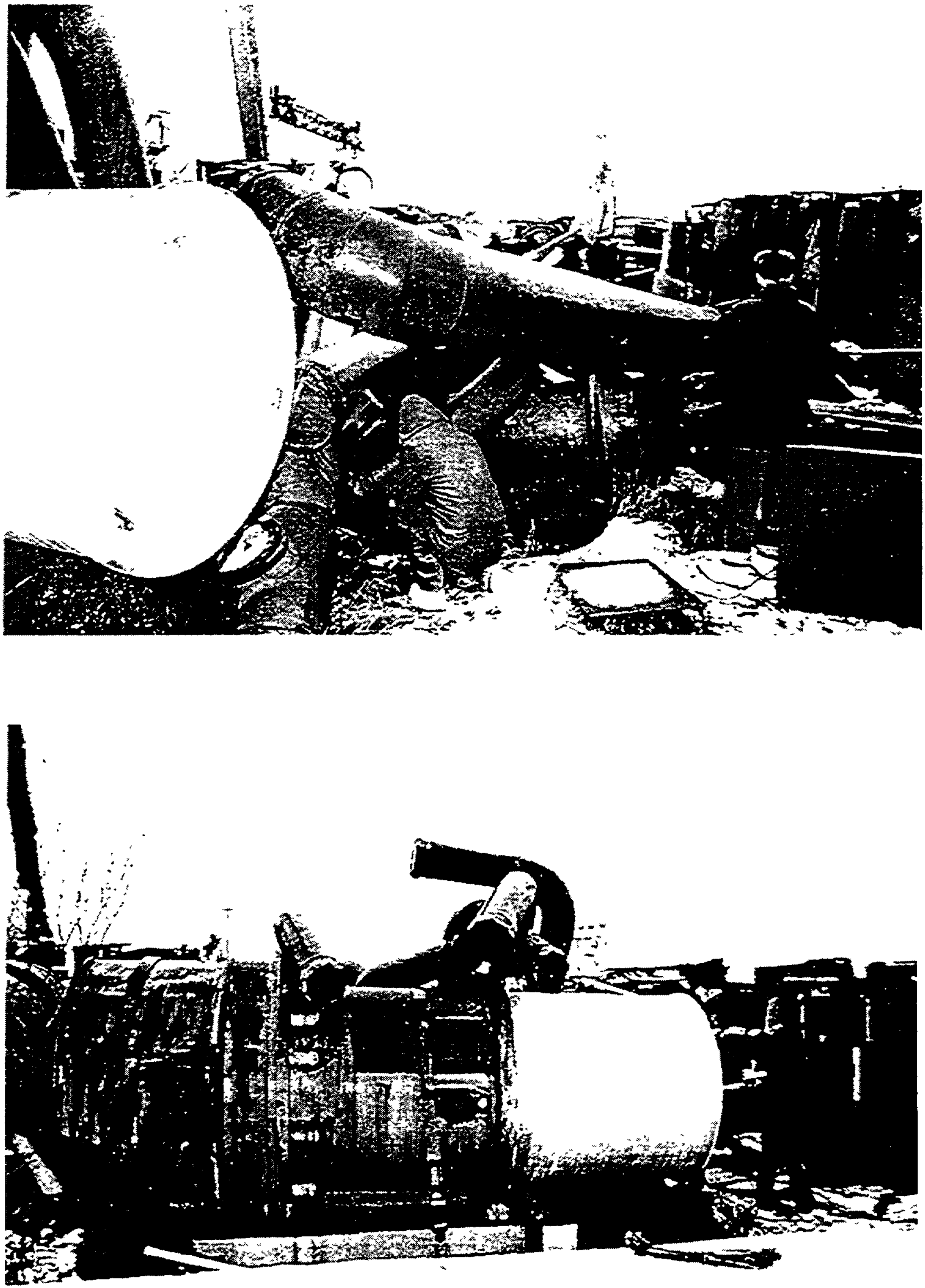
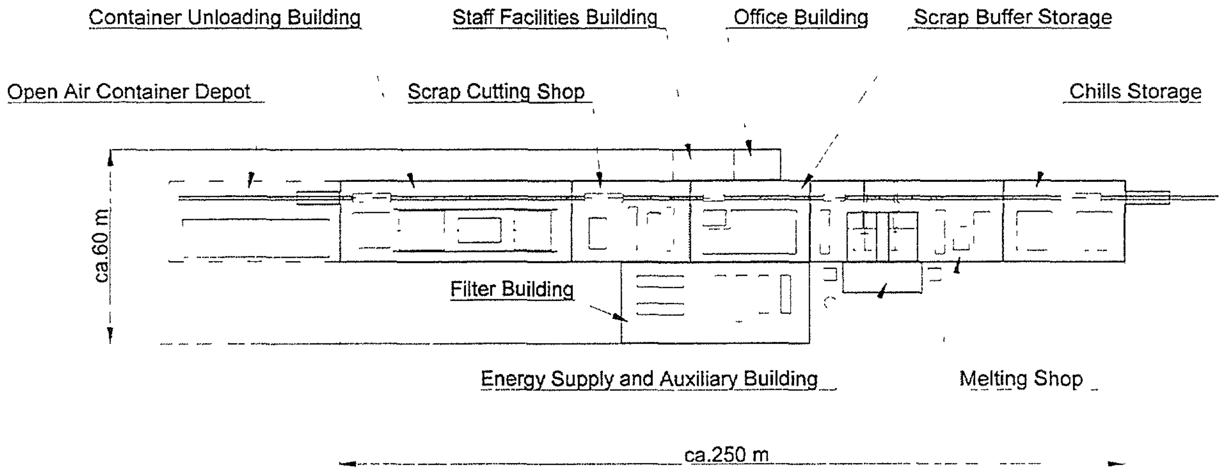


Fig. 2: Spare parts storage at Chernobyl NPP



melting aggregates:	1 induction furnace 1 electric arc furnace
melting capacity:	*10.000 t/a*
filter capacity:	390.000 m³/h
power requirement:	20 MW

Fig. 3: Main data and general arrangement of the SURF plant

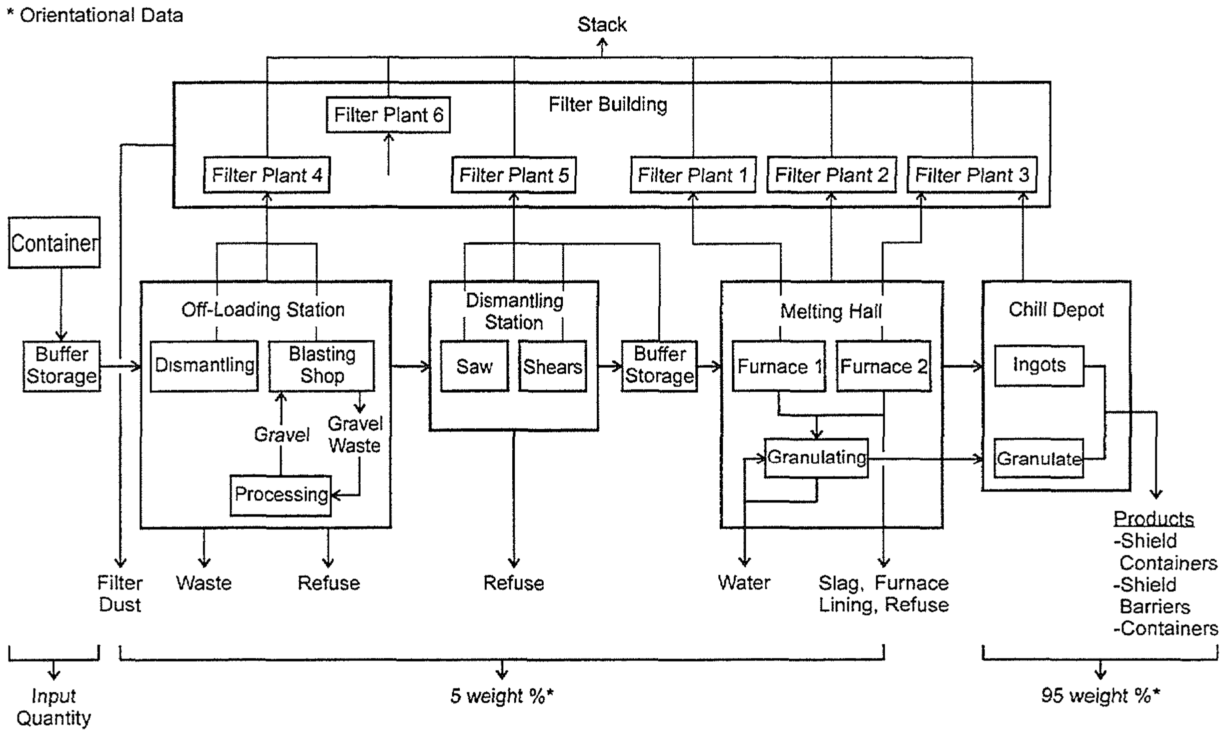


Fig. 4: Material flow diagramme of the SURF plant

The main elements of the SURF plant can be roughly described as follows:

- The melting shop:
In order to ensure a high degree of availability and with regard to the expected broad range of incoming material and their dimensions, two different furnace types have

been planned for, i. e. an induction and an electric arc furnace. Crucible induction furnaces which are operated at medium frequency are the ideal melting aggregate for bulky parts composed of various materials. The advantage of the discontinuously charged electric arc furnace lies with its specific larger crucible diameter which permits charging with larger pieces of scrap. For redundancy reasons both furnaces are housed in separate low-pressure enclosures each with their individual filter technology. They are controlled from a joint control station.

- The blasting shop:
All incoming materials ought to be blasted prior to further treatment, especially in order to cover highly contaminated parts. Blasting takes place in a tight enclosure where a negative pressure is produced by strong suction, so that no dust particles can escape to the outside.
The blasting material envisaged is medium grain-sized steel shot which has good stripping qualities.

- The granulator:
As an alternative utilization concept for the cast iron granulating is implemented (see chapter 3.2).

- Main auxiliary systems:
The air is filtered by 6 simultaneously operating filter systems with an overall discharge rate of 390,000 m^3/h. The filter systems for the blasting shop, the cutting area and the furnace casings consist of a high efficiency cyclone, a bag filter and a HEPA-filter and meet nuclear standards.
Besides torch-cutting devices two saws are foreseen for the cutting-up of thick-walled parts such as e. g. shafts. The main equipment is a heavy-duty hydraulic scrap shear with a cutting force of approx. 600 Mp.
The transportation system consists of a single track which covers the whole length of the plant. Flat trolleys battery-operated run on this track.

- Radiation protection concept:
The melting plant has been planned under consideration of the ALARA principle. This means that all radiation exposure is kept <u>a</u>s <u>l</u>ow <u>a</u>s <u>r</u>easonably <u>a</u>chievable under consideration of economic and social factors.

Possible danger to the personnel of the melting plant exists in form of external exposure from the contaminated scrap as well as the incorporation of radionuclides during handling. To minimize the exposure risk special clothing and wearing of breathing masks (type P 3) are required for work areas with higher radiological impact.
Model calculations have shown that even under conservative assumptions regarding α-activity the dose rate can be evaluated as very low in comparison with the annual dose limits of 50 mSv/a defined for the category A personnel working in the Chernobyl area.

3.1.3 Licensing requirements

Under consideration of the legal requirements, the CARLA plant with its supplementary facilities at Siempelkamp's Krefeld location has been confirmed as a pilot technique. This procedure assured a direct know-how transfer and enabled the implementation of the German licensing know-how.

Consequently, the Ukrainian authorities approached the German local licensing authority, the Bezirksregierung Düsseldorf, for assistance and consultant tasks, especially to obtain a formal statement on licensibility of the technical equipment of the SURF plant according to German regulations. The adaptation to the specific Ukrainian conditions and the formal licensing procedure would then be covered by the Ukrainian authorities.

The joint adjustment of the main design criteria was successfully elaborated on as can be shown with Fig. 5 giving the basic compilation of design requirements for the SURF plant in comparison to the CARLA values.

3.1.4 First licensing steps

According to the Ukrainian regulations the formal detailed plant licensing application has to be preceded by the licensing of the plant site on the basis of an assessment of three potential sites. Main criteria are safety aspects and infrastructural issues, but also technical-economic topics.

Fig. 6 shows the three assessed sites around the power plant area. As result of the detailed evaluation site option 3 has been selected, where especially advantages for the erection of the overall waste handling centre gave the decision.

On the basis of all the boundary conditions described above a licensing file has been elaborated consisting of the technical plant concept and a detailed description of the safety characteristics with main emphasis on radiation protection activities. The German local authority attested the licensability according to German regulations. This led to the initiation of the formal licensing procedure by the official application placed on December 28, 1995. Within 1996/1997 detailed discussions with the Ukrainian authorities took place giving their positive expertise. As last step before further project activities can be launched an official statement of the Ukrainian board of Ministries is needed. This statement should help to finalize the establishment of an adequate financing concept for the initiation of the erection period.

3.2 DEVELOPMENT OF GRANULES PRODUCTION TECHNIQUE

3.2.1 Motivation

Scrap with high chromium and/or nickel content is not suitable for recycling by casting of high-quality waste containers, as these constituents reduce the material toughness of the final cast iron products. Therefore, alternative recycling paths have to be used.

Furthermore, in general extension of application fields for melted material has been aimed for.

Subject		Design values	
		CARLA	SURF
1.)	Handling	200 Bq/g α, β, γ 100 Bq/g U 233, 235, Pu 239, Pu 241 (fission material) open and sealed 1000 Bq/g „naturally" contaminated materials	1000 Bq/g 1000 Bq/cm²
2.)	Utilization after melting		
a)	within the nuclear field	200 Bq/g α, β, γ 100 Bq/g fissable	1000 Bq/g 100 Bq/g fissable
b)	released	old: 1 Bq/g α, β, γ new: 10^{-4} A_{Fr} Bq/g (Residue regulation)	α: 7,4 Bq/g β, γ: 74 Bq/g
3.)	Waste (slag, dust, furnace lining)	old: 5 Bq/g released new: 10^{-4} A_{Fr} Bq/g i.e. Co 60: 5 Bq/g	7,4 Bq/g α 74 Bq/g β, γ
4.)	Exhaust air	10^{-6} A_{Fr} (Bq/m³) i.e. Cs 137: 0,5 Bq/m³ Co 60, Sr 90: 0,05 Bq/m³	0,15 Bq/m³ α, β, γ
5.)	Liquid waste	not applicable	optional: Granule waste water into NPP liquid waste system
6.)	Dose rate	1,5 rem/a 15 mSv/a (2000 h/a)	5 rem/a 50 mSv/a (only Cat. A required) (1700 h/a)
7.)	Areas		
	Surveillance area	x	-
	Control area	x No prohibited area Full protection during open handling	x No prohibited area Full protection during open handling
8.)	Throughput	4000 t/a	20000 t/a
9.)	BImSch		
	Dust	≤ 1 mg/m³ (Law: ≤ 20 mg/m³)	20 mg/m³
	Noise	55 dB	80 dB
	UVP	No	Yes
CO, No_x, SO_2 negligible		x	x

*) A_{Fr} = free limit for activity

Fig. 5: Design requirements for the SURF plant in comparison to the CARLA values

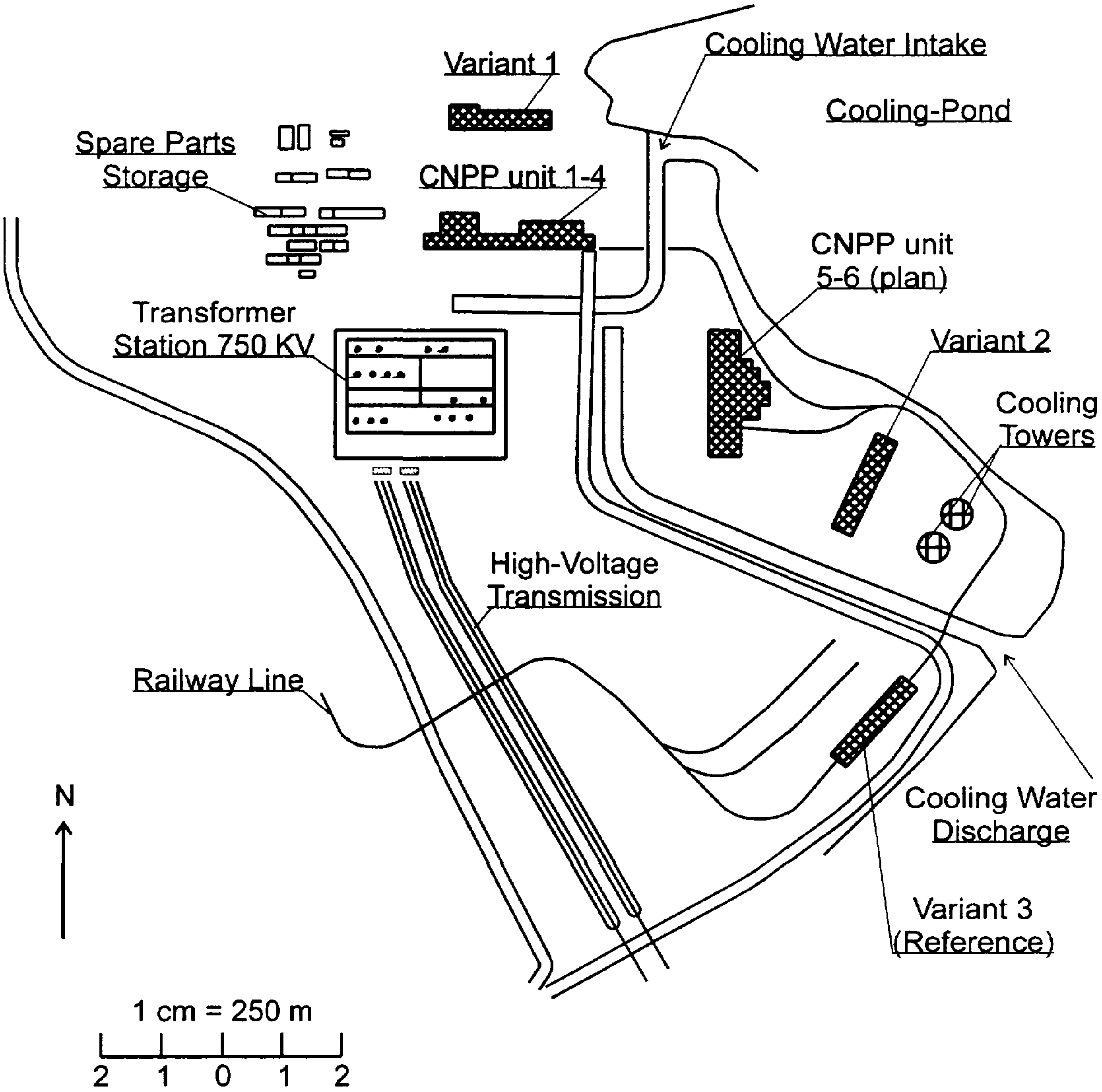


Fig. 6: Site variants for the SURF plant

Both goals led to the final detailed development of the granules production technique to substitute the hematite portion in concrete structures, like shielding containers or shielding structures for different purposes.

3.2.2 Technical basic work

Based on first research work in the early 1990s at the Dutch engineering company A+ [3] Siempelkamp has performed tests on a technical scale since 1995 to confirm the suitability of steel granules for the production of shielding equipment.

The main process step is given by the injection of the melt into a horizontal water jet, where the iron melt is spread into small drops solidifying at once in a water bath (Fig. 7).

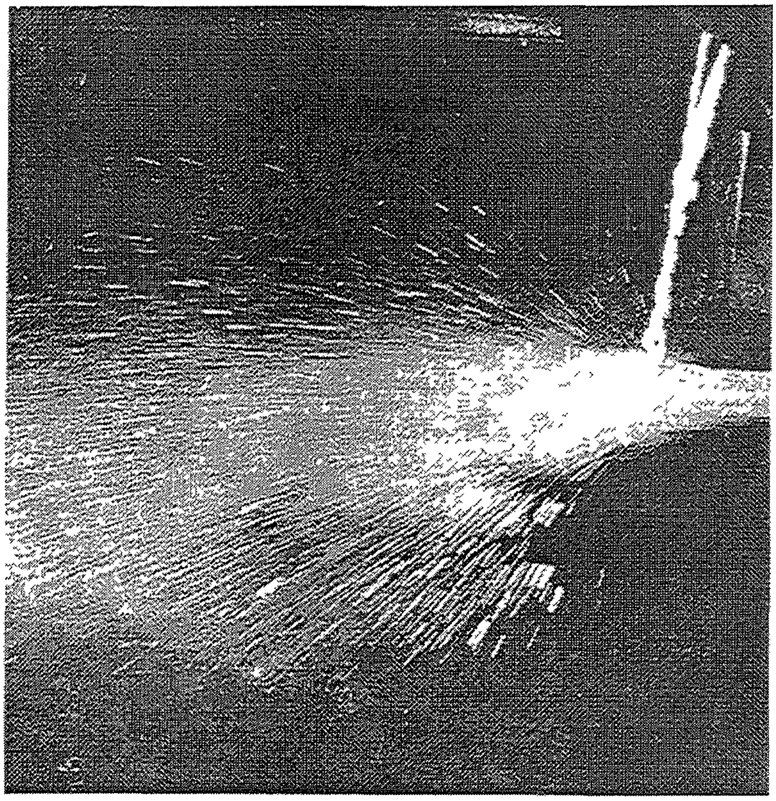


Fig. 7: Granulating of metallic melt

The following main results were gained:

- Approx. 50 wt.% of the concrete structure can be substituted by recycled granulated scrap;
- demanded density in the range of 3.5 kg/dm³ and compression strength of 45 N/mm² can be met;
- uniform distribution of the granules can be realized, guaranteeing for sufficient shielding efficiency;
- shape and grain size of the granules mainly depend on chemical composition of the scrap material as well as the casting and water jet velocity.

3.2.2 Optimization of the large-scale production process

The promising test results led to the initiation of the optimization phase for the large-scale production process and of the formal qualification procedures for generation of shielding equipment [4].

As first step production of granules using radioactively contaminated metal scrap under conditions in a controlled area was established. For this purpose, a special facility mainly consisting of the melt pouring system, the water injector, the granules sieve and a 20 m³ water basin was erected within the CARLA plant (Fig. 8).

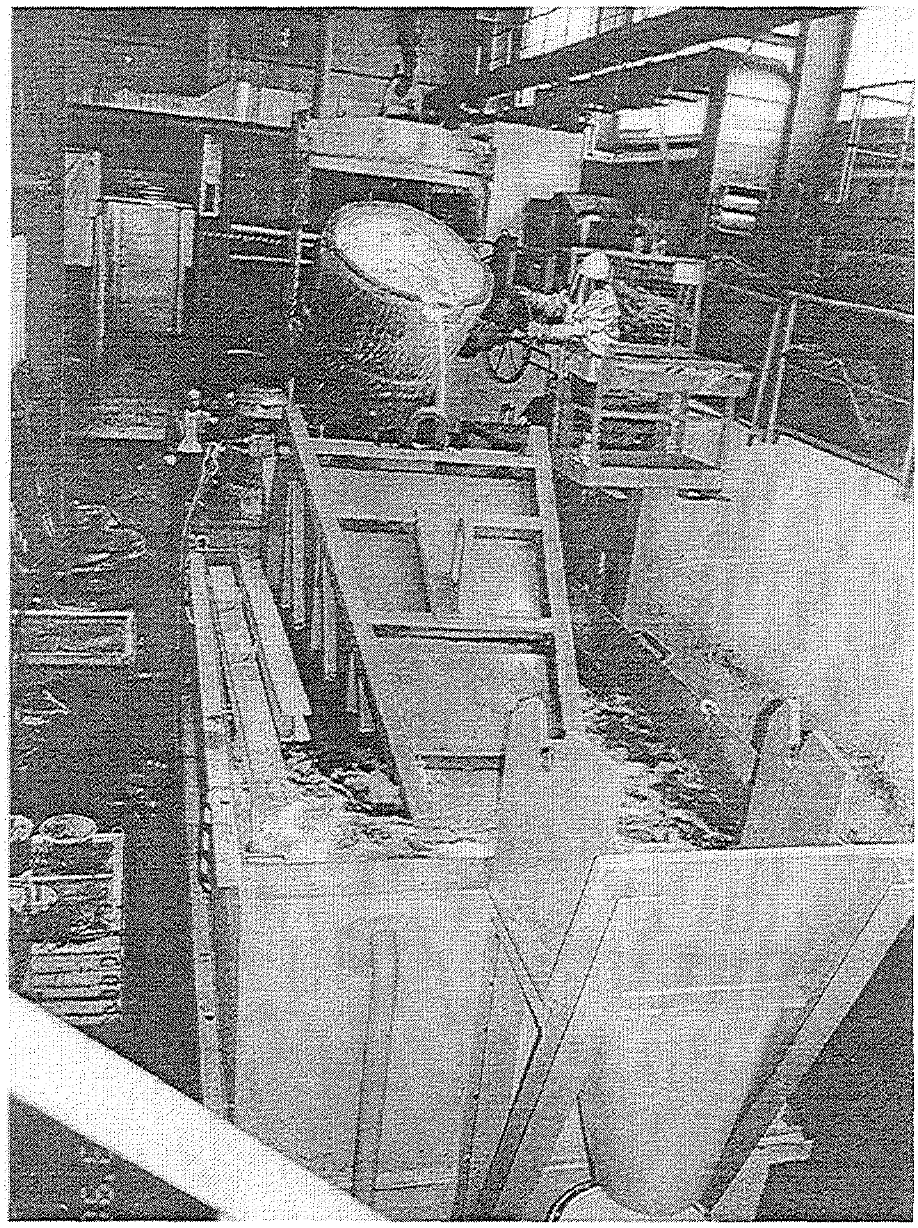


Fig. 8: Granules production in Siempelkamp's CARLA plant

The goal set up was to obtain spherical solid granules with diameters between 1 mm and 8 mm for optimization of a homogeneous vertical distribution and therefore uniform shielding efficiency in the container walls to be produced. Fig. 9 shows a typical sieve analysis obtained.

A reference generation rate of 2-3 Mg/h could be derived based on a „normal" CARLA plant operation with a melt temperature of approx. 1500°C, a water pressure of 0.5 bar and an average granulating period of 15 min. per 3 Mg melt. It could be shown that final drying of the granules minimized corrosion and agglomeration of the granules.

As sample product for the granulation technique a concrete shielding container (type SBA 200) for 200 l drums was defined, implementing 1.4 Mg of granules equivalent to 50 wt.%.

The granules were charged into a mobile concrete mixer filled with the basic concrete mixture. After mixing for 15 minutes the granule concrete was filled into a special permanent mould. Already some minutes later on, the permanent mould could be removed. Fig. 10 shows the view into a typical granule concrete shielding container gained by this procedure.

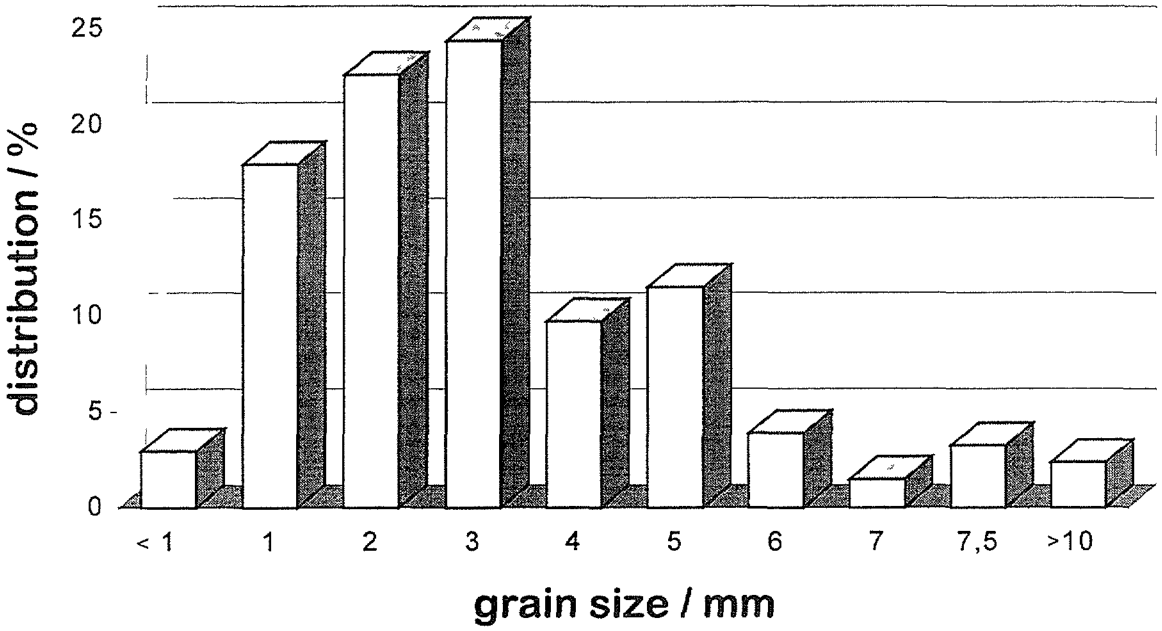


Fig. 9: Typical sieve analysis of the granules production

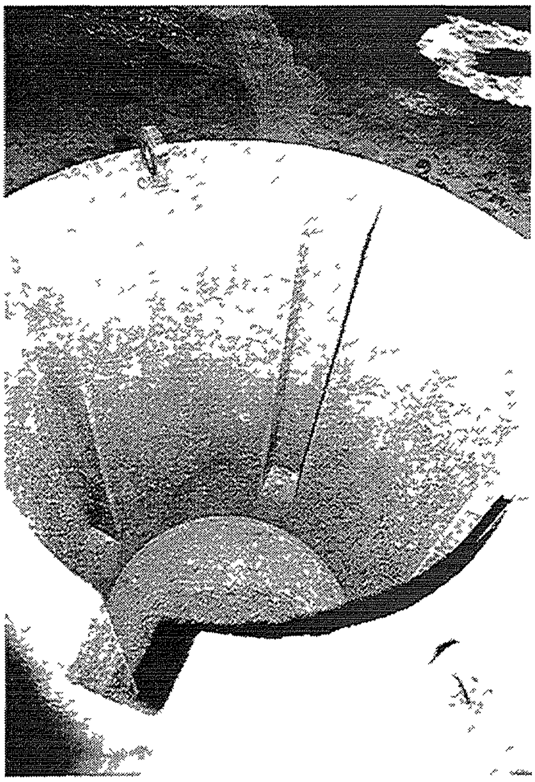


Fig. 10: Granule concrete shielding container for 200 l drums

It could be attested that the requested bulk density of 3.5 kg/dm³ could be obtained as well as the defined lower limit for the compressive strength of 45 N/mm² could be exceeded. Fig. 11 demonstrates a sufficiently uniform shielding effect during a check by making radiographs from the outside of a container with a Co 60 test source inserted.

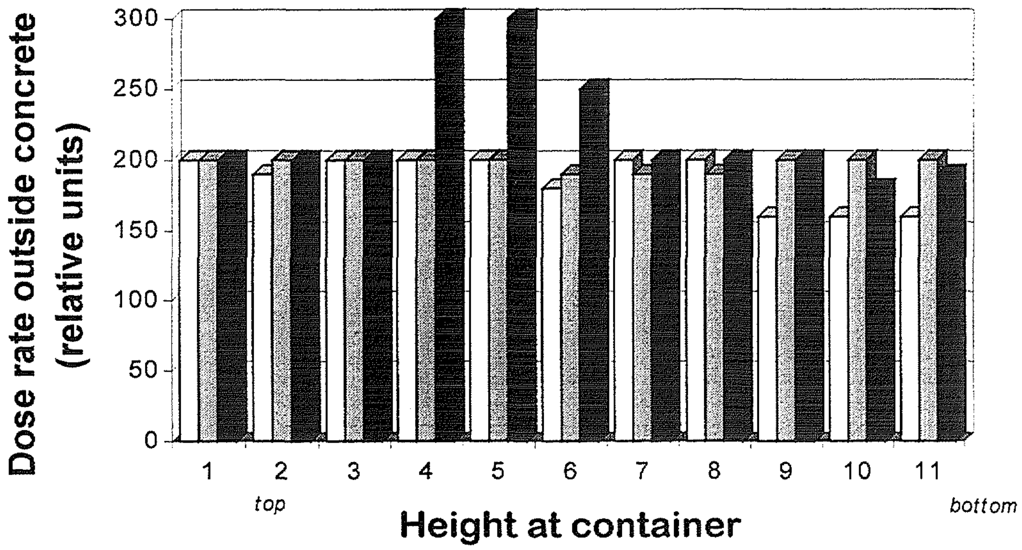


Fig. 11: Homogenity of radiation transmission of granule concrete shielding container (3 measurements per height level)

3.2.3 Formal qualification

For official attestation of the granule concrete shielding container all necessary tests for the so-called type A approval were performed at the beginning of 1997. An impression of the 1.2 m drop test according to the IAEA requirements is provided by Fig. 12. The component integrity was kept without any problems.

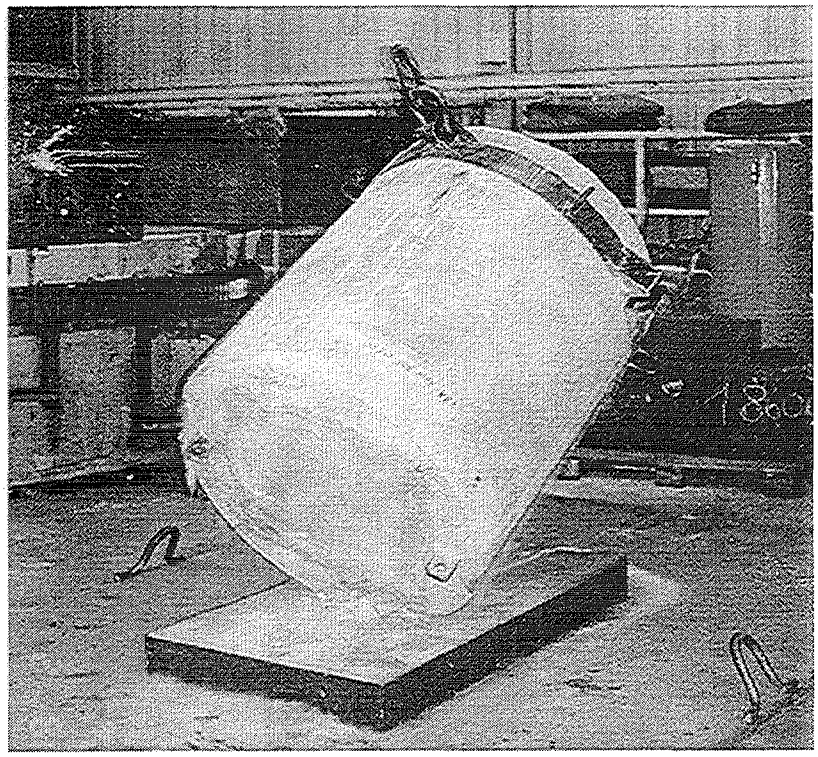


Fig. 12: 1.2 m drop test

To get the approval for the German final depository Morsleben (ERAM) the thermal conductivity of the granule concrete had to be measured. Assuming the worst case the thermal conductivity was 1.6 W/Km, a value which is low enough concerning a minimal container wall thickness of 140 mm.
After these successful tests the German authorities gave their approval.

4. CONCLUSIONS

With the melting technology an adequate safe method for decontamination and recycling of radioactively contaminated metallic scrap is available to be used for support of the remediation and decommissioning work at the Chernobyl site. By means of casting of high-quality waste containers as well as of granules production for manufacturing of granule concrete elements a broad field of reuse methods can be applied, especially attractive for the conditions of this specific area.

REFERENCES

[1] Proceedings of the Commission of the European Community's „Technical Seminar on Melting and Recycling of Metallic Waste Materials from Decommissioning of Nuclear Installations"
Krefeld/Germany, October 1993

[2] Steinwarz, Sappok
SURF - The melting facility for Chernobyl using CARLA-experience
Proc. ICONE5, Nr. 2258
May 26-30, 1997, Nice/France

[3] Lichtenberg et al.
Recycling of activated/contaminated reinforcement metal in concrete
Final Report, EUR 15045 EN, 1994

[4] Holland, Sappok
Production of granule concrete as an alternative recycling path for radioactive steel scrap
Proc. of the 3rd European Seminar on „Melting and Recycling of Metallic Materials from Decommissioning"
Nyköping/Sweden, June 1997

QUALIFICATION OF A LOW CONCENTRATION METHOD FOR DECONTAMINATION OF PRIMARY SYSTEMS

XA9847487

J. SCHUNK
Paks NPP

J. MAKAI, J. KREISZ, A. KRÓJER, P. KOMÁROMI, I. SCHREMMER
GIC Ltd

T. SZÁNYA, L. HANÁK, G. SIMON
Veszprém University

Hungary

Abstract

In early nineties a research and development project was initiated to work out a full primary system decontamination technology. The main goal of the RD project was to develop a low concentration, "soft" decontamination technology that can be fitted well to PAKS NPP's system. The most important requirements are to achieve a decontamination factor as high as possible, a low corrosion rate, and the use of chemicals that can be treated by simple methods as liquid waste.

During past years we investigate LOMI type solutions containing V(II), Cr(II) ions as reducing agents, and gluconic acid as complexing agent, comparing to the EDTA and other complexant containing solutions. First of all we made some comparative tests with EDTA and picolinic acid solutions containing V(II) and Cr(II) compounds. After that a more detailed test were carried out with EDTA containing decontaminating procedures in laboratory scale. On the base of laboratory tests we got license from the Hungarian Nuclear Safety Inspectorate to use this technology in practice at Paks NPP (steam generators' decontaminations were done. In this time the waste treatment became one of most important question to be solved. The goal of the waste treatment project was to develop a selective ion-exchange-sorption technology using a system with removable cartridges. A layered fixed bed technology was developed. This system is under detailed design and preparation of implementation phase.

During the last year we continued the work with detailed investigation of corrosion layer oxidising technology and the preparation of full system decontamination qualification programme was also started with technological summaries and working out of the material balance of Paks NPP's primary systems. In the investigation of oxidising technology the alternative of the alkaline-permanganic oxidation was studied. We have investigated various solutions of permanganic acid for oxidation of corrosion layers. Inactive tests were carried out on stainless steel samples with spinel oxide on their surface that was prepared by high temperature wet method. After inactive laboratory tests we have tested the oxidation technology on active samples.

We also investigate the corrosion effects of the oxidising and reducing solutions e.g. taking polarisation curves by voltametric methods.

We have also investigated the possible use a combined electrochemical method for preparation of permanganic acid. The treatment and decomposition of gluconic acid waste is simpler than that of EDTA containing decontamination waste solution.

Further investigations have to be done for studying the corrosion behaviours of the decontaminating solutions and the after decontamination passivation of the treated surfaces to prevent the increased corrosion product dissolution during starting and further operation of reactors.

Introduction

As it is well known, in PWR plants, the corrosion layer removal during the plant decontamination requires at least a two-step process because of the chemical properties of the oxide layer.

- In first step the oxidation of the corrosion layer is necessary due to the more than 20% of its chromium content that is insoluble in Cr^{3+} form;

- In the second step the removal of the oxidised corrosion layer should be carried out. This is an acidic and/or reductive dissolution of the oxide. The iron content of the oxide is more soluble in Fe^{2+} form.

In the technical design of WWER 440 type the proposed full system decontamination technology includes the following steps

First step: oxidation of chromium rich oxide layer with solution of

~ 10 g/dm^3 NaOH
~ 5 g/dm^3 $KMnO_4$
~ Temperature of the solution is 100°C

Second step: the removal of the traces of the permanganic ions and MnO_2 precipitate from the solution and from surfaces

~ 30 g/dm^3 oxalic acid
~ Temperature of the solution is 100°C

Third step: dissolution of oxidised corrosion layer

~ 10 g/dm^3 oxalic acid
~ 10 g/dm^3 citric acid
~ 1 g/dm^3 HNO_3
~ Temperature of the solution is 100°C

Considering this technology high enough decontamination factors can be achieved but it has some disadvantages in full system decontamination application. They are the followings:

- This technology has no references and experiences in the field of full system decontamination;
- Due to the high concentration and the properties of the chemicals, simple waste treatment (e.g. ion exchange) can not be used;
- Possibility of stress corrosion due to the application of oxalic acid.

The above mentioned statements gave the reasons for the development a low concentration – so called "soft" –decontamination technology. The main requirements for the full system decontamination are the followings:

- Achieve a decontamination factor as highs as possible;
- Acceptable corrosion rate of the all wetted structural materials during the whole decontamination process;
- Low demands of chemicals to achieve good or acceptable decontamination factors (DF);
- Generate easy to treat radwaste generated during the decontamination that can be treated by simple method for example ion exchange or sorption.

Decontamination step development

In the past years we have dealt with the second decontamination step in which we use V(II) and Cr(II) compounds as reducing agent, and EDTA or gluconic acid as complexing chemical as well. We made comparative test with solutions that contain picolinic acid as complexing agent as well. Because picolinic acid is quite expensive reagent, the further research work was focused on the usage of EDTA, because it is a commonly used reagent in the decontamination and chemical cleaning of corroded stainless steel and mild steel surfaces

One of the most important tasks was the production of the chemicals in the required quantity and quality. After several years of efforts PAKS NPP and G.I.C. LTD have developed a special electrochemical technology for the production of stable V(II) and Cr(II) complexes in crystalline form in a joint project. The first investigations of applicability of these compounds in decontamination process have been carried out using EDTA as complex forming ligand and magnetite for model compound taken directly from the secondary side of the SG. On the next table the comparative results of magnetite dissolution can be seen.

Table 1: Magnetite dissolution results in laboratory scale experiments

Treatment time (minutes)	**Dissolved magnetite concentration in laboratory scale experiments (mg/dm³)** (Temperature 70°C, pH = 4-4,5 adjusted by hydrazine-hydrate and ammonia)				
	0.03 M pic. acid 0.002 M V^{2+}	0.03 M pic. acid 0.004 M V^{2+}	0.06 M pic. acid 0.004 M V^{2+}	0.01 M EDTA 0.002 M V^{2+}	0.01 M EDTA 0.002 M V^{2+} 0.02 M Cr^{2+}
30	200	300	300	360	460
60	200	440	360	460	440
90	280	500	360	540	480
120	300	500	400	740	520
150	360	500	460	820	500
180	400	500	520	900	520

Having found that the above mentioned system is suitable for the said purpose it was successfully used in test steam generator decontaminations in 1993 and 1995 at Paks NPP.

In the following tables some results of decontamination carried out in 1995 at unit No. 2, on steam generator no. 4 are presented. This decontamination procedure was carried out in two cycle. The step s of two cycle are summarised in the followings:

A. Oxidation with alkaline permanganate solution (10 g/dm³ NaOH and 5 g/dm³ $KMnO_4$) on 90°C;
B. Flushing with clean condense water;
C. Reductive treatment with solution containing 0.005 mol/dm³ V^{2+} ions and 0.05 mol/dm³ EDTA on 90°C;
D. *Acidic treatment with 10-10 g/dm³ citric acid and oxalic acid on* 90°C;
E. Flushing with 1 g/dm³ H_2O_2 solution;
F. Flushing with 5 g/dm³ ammonium-hydroxide solution
G. Flushing with clean condense water.

Table 2: Results of test decontamination was carried out in 1995 on unit 2, SG 4

First cycle

	Activity concentration of decontaminating solution (Bq/dm³)							**Concentration of metals in decontaminating solution (mg/dm³)**					
Step	**^{51}Cr**	**^{54}Mn**	**^{59}Fe**	**^{58}Co**	**^{60}Co**	**^{110m}Ag**	**Total**	**Fe**	**Cr**	**Ni**	**Co**	**Mn**	**Total**
A	1.21e6	1.28e6	6.75e3	3.23e3	3.38e3	5.03e5	3.01e6	0	59.3	0	0		59.3
B	1.00e3	4.99e3	2.00e2	1.38e3	1.10e3	7.38e3	1.61e4	0.36	3.45	0.1	0		3.91
C	4.68e5	2.09e6	1.56e6	1.23e7	1.66e7	4.57e4	3.31e7	402	3.21	42.0	0.3	24.13	471.64
D	6.65e0	2.22e6	1.62e6	1.28e7	1.77e7	3.42e5	3.42e5	714	8.17	28.36	0.04	4.57	755.14
E	1.43e5	9.10e4	3.82e4	3.44e5	2.23e6	3.40e5	3.40e5	-	-	-	-	-	-
F	1.29e5	4.52e4	1.98e4	7.43e4	4.93e5	1.95e5	1.95e5	-	-	-	-	-	-
G	3.63e4	2.13e4	1.16e4	2.06e4	1.64e5	4.93e4	4.93e4	2.64	0.11	1.49	0.02	0.05	4.31

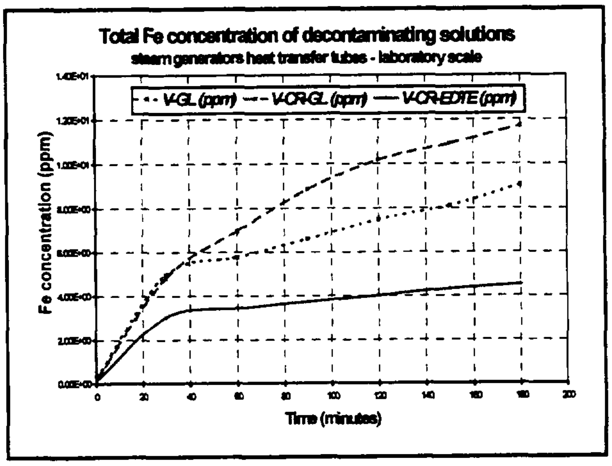
Second cycle

	Activity concentration of decontaminating solution (Bq/dm³)							**Concentration of metals in decontaminating solution (mg/dm³)**					
Step	**^{51}Cr**	**^{54}Mn**	**^{59}Fe**	**^{58}Co**	**^{60}Co**	**^{110m}Ag**	**Total**	**Fe**	**Cr**	**Ni**	**Co**	**Mn**	**Total**
A	1.65e5	1.80e5	4.28e3	1.26e4	1.43e5	1.32e5	6.37e5	0.00	59.30	0.00	0.00		59.3
B	1.97e5	1.95e4	3.30e3	2.91e4	2.12e5	3.57e4	4.97e5	0.36	3.45	0.10	0.00		3.91
C	2.15e5	3.80e5	8.29e4	1.75e6	1.06e6	7.30e5	4.22e6	402.00	3.21	42.00	0.30	24.13	471.64
D	1.82e5	1.09e5	8.13e4	5.29e5	7.60e6	4.47e5	8.95e6	714.00	8.17	28.36	0.04	4.57	755.14
E	1.82e5	8.32e4	5.42e4	2.69e5	3.25e6	5.11e5	4.35e6	-	-	-	-	-	-
F	2.33e5	3.58e4	3.98e4	1.29e5	1.51e6	3.38e5	2.29e6	-	-	-	-	-	-
G	1.64e5	2.91e4	3.49e4	1.29e5	1.14e6	2.30e5	1.73e6	2.64	0.11	1.49	0.02	0.05	4.31

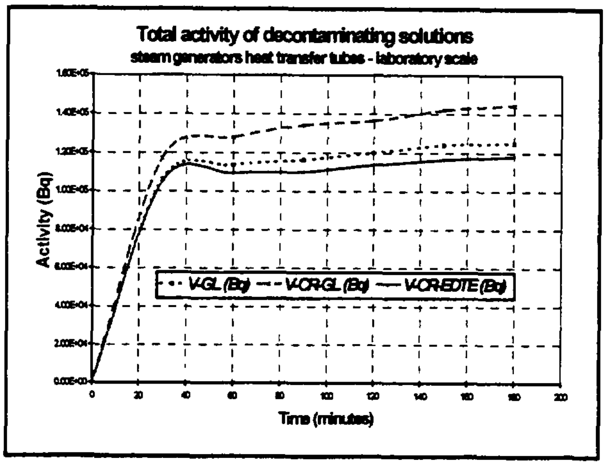
The data show that the activity removal (considering the ^{60}Co, ^{58}Co and ^{110m}Ag) almost the is same in the reductive treatment with V(II) containing solution and CITROX solution as well. But considering the dissolved metal quantities it can be stated that the Fe removal in CITROX step is more efficient that in reductive step.

Using of EDTA brought up the problem of its radiolysis leading to undesirable, corrosive decomposition products. Laboratory experiments have been carried out in order to investigate the possibility of replacement of EDTA with the radioactivity-resistant gluconic acid using both magnetite and pieces of contaminated heat transfer tubes taken from the SG. In the latter case it was also examined, how the incidentally remaining spinel type metal oxides can effect the decontamination process if the alkaline oxidation or the acidic treatment should not be completed prior to it.

The next figures show the results of the laboratory scale test decontamination that was carried out on heat transfer tubes of steam generators. The used decontaminating solutions were V(II) and gluconic acid (V-GL), V(II), Cr(II) and gluconic acid (V-CR-GL) and V(II), and Cr(II) and EDTA (V-CR-EDTA). The oxidising pre-treatments were carried out with alkaline permanganate.



1. Figure: Comparative test with gluconic acid, EDTA and V(II) containing solutions (Fe)



2. Figure: Comparative test with gluconic acid, EDTA and V(II) containing solutions

In this test solutions containing gluconic acid and reductive agent (V(II) or V(II) and Cr(II) as well) seem to be efficient if we consider both the activity and corrosion layer removal. In these test we replace the ammonium-vanadium(II)-sulphate with vanadium(II)-gluconate. The chromium(II) was used in the acetate form. This changing of sulphate ligand is due to the aim of avoiding or decreasing the corrosive effect of sulphate ions.

Improvement of the contaminated layer oxidation

One of the most important factors of the efficient decontamination of the PWR plants is the oxidation of the chromium rich oxide layer on the surfaces. Alkaline permanganate has been used previously in the practice at Paks NPP and in our experiments.

We have planned to find a more effective oxidation process that can be used before EDTA or gluconic acid, V(II) and Cr(II) solution as the decontamination step. The main goal was to achieve better decontamination effectiveness and less waste sludge from the MnO_2, generated in the oxidation process. The problem is that, this sludge can settle down in primary surfaces and dead places hindering the following decontamination step effectiveness.

Inactive laboratory tests with simulated oxide layer (08H18N10T type stainless steel tube in high temperature furnace and wet inert gas) and active laboratory tests with real contaminated samples were carried out during this step of our development work.

The following reagents were tested in the inactive laboratory pre-qualification test.

- Alkaline potassium-permanganate;
- Permanganic acid;
- Sodium-peroxoborate.

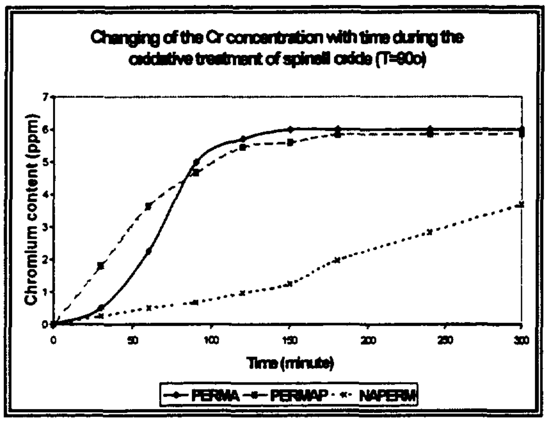
During the oxidation test the concentrations of the oxidising agents were varied to achieve the optimal conditions for the oxidation of the layer. The tests were carried out in a completely stirred tank reactor. The temperature of the oxidation was 90°C in every case and was controlled with a thermostat.

After preliminary tests the following oxidising solutions were selected for further test:

- AP solution containing 0,035 mol/dm^3 potassium-permanganate and 10 g/dm^3 sodium-hydroxide, that is the commonly used solution in WWER plants;
- Permanganic acid in concentration of 0.035 mol/dm$_3$, containing 0.35 mol/dm^3 H_3PO_4;
- Sodium-peroxoborate ($NaBO_2 H_2O_2 3H_2O$) in concentration of 0.0875 mol/dm^3.

The permanganic acid was prepared by a laboratory scale electrochemical method. In permanganic acid solution 50 ppm K^+ ions remained. The necessary proton concentration was adjusted by phosphoric acid. The phosphoric acid stabilises permanganic acid as well. This solution can be stored for longer period of time with only acceptable degradation of permanganate.

The oxidation steps were followed by washing of the surface of the specimens with various solutions for removing the MnO_2 precipitate and trace of the oxidising agents particularly the permanganic ions from the surface.



3. Figure: Inactive laboratory tests with oxidising solutions

Comments:
PERMA: permanganic acid
PERMAP: permanganic acid and phosphoric acid
NAPERM: alkaline permanganate

The washing solutions were the followings:

- Gluconic acid 20 g/dm^3;
- Citric acid 10 g/dm^3;
- Oxalic acid 10 g/dm^3.

The figure No. 3 represents the results of the inactive oxidising test on stainless steel specimens with spinel oxide.

The sodium-peroxoborate has no any effect on the surface oxide. With the permanganic acid the oxidation is more effective than with alkaline-permanganate solution. The phosphoric acid has no role in the dissolution of oxide layers because if we use high H_3PO_4 excess (ten times higher concentration than permanganic acid) a similar saturation curve can be realise as in the case of $HMnO_4$ solution with low H_3PO_4 content. The total chromium removal after 300 minutes was 6.00 ppm, 5.87 ppm and 3.69 ppm for permanganic acid, permanganic acid containing phosphoric acid and alkaline permanganate respectively.

The adjustment of the proton concentration by phosphoric acid has only slight effect on the rate of the reaction. The saturation curve means that there is no dissolution of the base metal. We have tested the effect of the permanganate concentration, because in the previous test only the 0.3 % of permanganate was consumed for the reaction. In these tests 40 cm^3 solutions were used for 1 cm^2 of the specimens.

The reaction rate for the Cr content in the solution proportional to the variation of permanganate content. We have stated that the reaction rate decrease with concentration, but the rate in alkaline-permanganate is lover than that of acidic permanganate solution diluted ten times. The MnO_2 precipitate is also generated in acidic oxidation, and its amount was proportionally higher with the increasing oxidation degree. In the presence of Mn(VII) and

Mn(II), the generation of MnO2 precipitate cannot be avoided, independently of the pH, due to the synproportion. The gluconic acid containing washing solution was fully acceptable for removal of precipitate.

The active tests were carried out on specimens made from a part of control rod drive mechanism. For the sake of the completeness we have done oxidative treatment followed by acidic washing for all tested samples. We have used the possible and preferred combinations of oxidative pre-treatments and washing solutions.

The tested, combined chemical treatment cycles were the followings:

- Alkaline oxidation, CITROX washing;
- Acidic oxidation, washing with gluconic acid;
- Alkaline oxidation, washing with gluconic acid;
- Acidic oxidation, CITROX washing.

Table 3: The activity of the samples treated with alkaline-permanganate and various washing solutions

Treatment		Sample activity (Bq/sample)			
		No. 2	No. 4	No. 5	No. 7
Activity Before Treatment	Mn-54	2380	1880	2680	2980
	Co-60	38900	42900	58900	61900
	Ag-110m	8890	5500	6600	7500
Activity after treatment with KMnO4	Mn-54	1750	984	1780	2080
	Co-60	5660	39900	56900	60900
	Ag-110m	2300	1800	1800	2000
Activity after washing with CITROX	Mn-54	54	-	-	61
	Co-60	450	-	-	340
	Ag-110m	940	-	-	490
Activity after washing with gluconic a	Mn-54	-	89	134	-
	Co-60	-	3060	5360	-
	Ag-110m	-	450	590	-

Table 4: The activity of the samples treated with permanganic acid and various washing solutions

Treatment		Sample activity (Bq/sample)			
		No. 1	No3.	No. 6	No. 7
Activity Before Treatment	Mn-54	2080	1880	2580	2680
	Co-60	38900	42900	60900	54900
	Ag-110m	8800	5500	7000	6900
Activity after treatment with HMnO4	Mn-54	534	564	844	704
	Co-60	5660	5260	11100	6560
	Ag-110m	130	910	1400	1200
Activity after washing with CITROX	Mn-54	-	144	204-	-
	Co-60	-	1365	2160	-
	Ag-110m	-	220	300	-
Activity after washing with gluconic a.	Mn-54	134	-	-	180
	Co-60	1260	-	-	1560
	Ag-110m	330	-	-	198

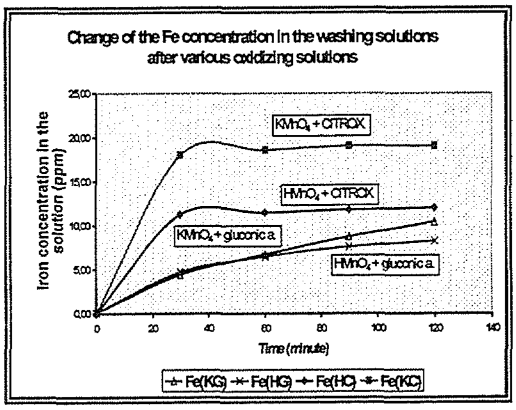
The acidic oxidation caused far higher activity decrease than the alkaline one. The MnO_2 generation was also more significant during the treatment with acidic solution. A loose precipitate was generated by acidic oxidation that can be easily remove by rinsing with demineralised water. The activity decrease in washing treatments is more significant after the alkaline oxidation. The reason is that, although the alkaline oxidation apparently less efficient, it degrades the spinel oxide layers but doesn't dissolve its component. In the alkaline solution an unbroken chromate film is formed which hinders the diffusion of the oxidising agent to the sample surface. In acidic solution the chromate film is dissolved and the Cr(VI) goes to the solution.

The Table 5 presents the decontamination factors calculated from the oxidation test activity data. The advantage of the acidic oxidation is doubtless. If we consider the DFs for two steps (oxidation and washing) together (DF3) the situation is not so clear. It is worth to mention the significant activity removal of Co-60 nuclide in acidic steps after alkaline oxidation. The test decontamination of steam generator is planed for real evaluation of the oxidation effectiveness (dose rate and surface contamination measurements are necessary).

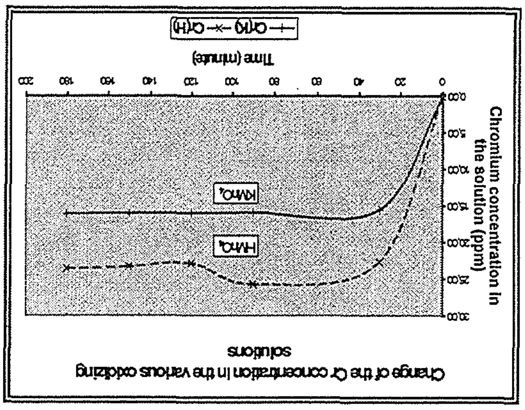
Table 5: Summary of the DFs calculated from the activity data presented in Table 2 and Table 3

		Sample ID							
		No. 1 SG	No. 3 SC	No. 6 SC	No. 8 SG	No. 2 LC	No. 4 LG	No. 5 LG	No. 7 LC
DF1	Mn-54	3.82	3.62	3.02	3.69	1.36	1.86	1.54	1.44
	Co-60	6.73	7.46	5.4	8.27	1.03	1.08	1.02	1.01
	Ag-110m	6.73	6.16	5.2	5.39	3.86	3.13	3.58	3.71
DF2	Mn-54	3.98	3.92	4.13	3.91	34.2	11.1	13.3	34.1
	Co-60	4.49	3.85	5.14	4.2	84.2	13.0	10.6	179
	Ag-110m	3.94	4.13	4.67	6.06	2.44	4.0	3.05	4.08
DF3	Mn-54	15.2	14.0	12.5	14.4	44.2	20.5	20.5	49.1
	Co-60	30.2	28.7	27.8	34.7	86.7	14.1	10.8	181
	Ag-110m	26.5	24.3	24.3	32.6	9.4	12.5	10.9	15.1

Comment: L alkaline oxidation; S acidic oxidation; G washing with gluconic acid, C washing with CITROX



4. Figure: Results of active laboratory test with oxidation followed washing of the MnO$_2$ precipitate (Fe content)



5. Figure: Results of active laboratory test with oxidation (Cr content of the solutions)

Some data of the active laboratory tests are presented on the figures No. 4 and 5. The concentration of chromium in the solution reached the maximal level practically after 30 minutes (saturation). The saturation is higher in the case of the acidic oxidising solution. If we consider the alkaline solution the possible maximal concentration is not reached because of the formation of the a chromate. The more significant decrease of permanganate was stated in the case of acidic solution. It is due to the stronger oxidising power of this solution. The recommended treating period is no longer than 60 minutes, because the main oxidising reaction is completed in the first 30 minutes. During this time there is no significant difference in MnO$_2$ generation of two solution.

The Ni and Fe cannot be detected in the alkaline solutions (by using of ICP) in contradiction to the acidic solutions. This is due to the cationic forms of these metals that cannot be dissolved alkaline solutions. In these tests the CITROX solution used after the alkaline oxidation removes most chromium. But this quantity is lover than the chromium content removed in acidic treatment. The total removed chromium in acidic oxidation is 23,57 ppm and 16.08 + 1,78 ppm in alkaline oxidation followed by CITROX washing.

During the test we stated that the MnO$_2$ can be dissolved quickly from the surfaces.

In the alkaline oxidation the iron did not go into the solution, but in the CITROX step the iron can be effectively dissolved from corrosion layer loosened by oxidation. The iron forms a stable and soluble complex compound with oxalate ion. This is why the iron content is higher in the CITROX solution after the alkaline treatment. The removed iron content in permanganic acid solution was 24.31 ppm. The total removed iron was 19.05 ppm during the alkaline oxidation followed by CITROX and 10.42 ppm if the second step is washing with gluconic acid. In the CITROX solution not only the removed iron content was higher but the rate of dissolution was faster as well.

In the case of nickel the situation is similar to iron, but it forms insoluble precipitate with oxalate ions.

Waste treatment developments

In the research project the treatment of the waste that potentially generated during the application of the full system decontamination was also an important programme. In this part of our RD project the Chemical Engineering Department of Veszprém University have the main role. They deal with the ion exchange – sorption technology development and chemical decomposition of liquid waste. In this field the G.I.C. Ltd. deals with the electrochemical and chemical decomposition of liquid decontamination waste and their combination of ion exchange and sorption processes. The degradation of contaminated ion-exchanger and sorption materials is studied as well.

In the ion exchange–sorption studies, the treatment of alkaline-permanganate and the citric acid-oxalic acid containing solutions were tested. As the result of inactive laboratory scale tests followed by active laboratory scale test and pilot-plant test, a multi-layered selective ion-exchange-sorption process was developed. The process based on the reactive adsorption on a pre-treated charcoal layer followed by the sequential usage of the pre-treated cation and anion exchanger layers. In the laboratory scale test the reactive adsorption process was modelled.

The next tables and figures represent the column efficiency for the activity removal from the alkaline-permanganate oxidising and citric acid and oxalic acid containing decontaminating solutions.

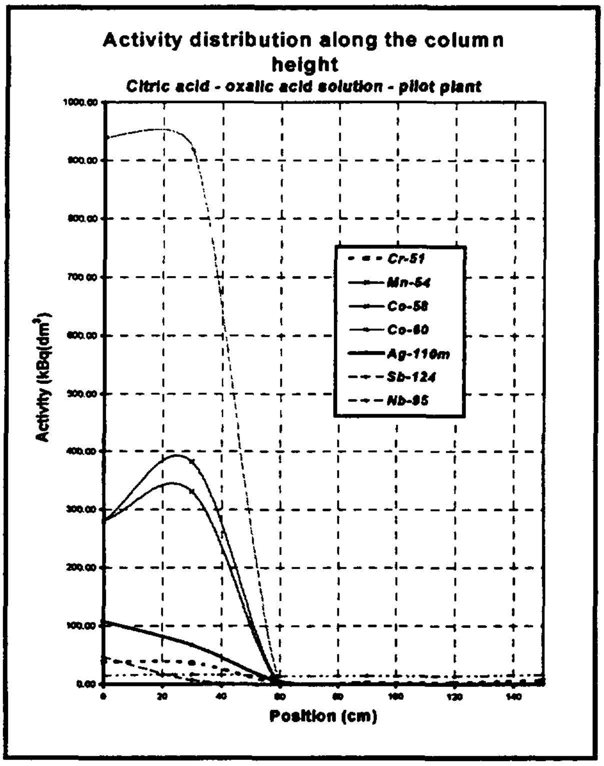
The temperature of the columns was 95°C controlled by a thermostat. The concentration of the alkaline-permanganate solution was 10 g/dm^3 NaOH and 5 g/dm^3 $KMnO_4$, and that of acidic decontaminating solution was 10-10 g/dm^3 citric acid and oxalic acid respectively. The real decontaminating solutions gained from main circulating pump (primary cooling pump) and steam generator decontamination were used during the test. The main goal of the test was to reduce the activity concentration of the relevant radionuclides below 1 kBq/dm^3. The most important nuclides are ^{60}Co, ^{54}Mn and ^{110m}Ag. Other requirement for the system to be developed was that the system shall be a moveable, cartridge system with capacity that is enough to treat waste generated during the decontamination steam generators with alkaline oxidation followed by an reductive or CITROX treatment.

Table 6a: Decontamination waste treatment tests with layered ion exchange sorption system

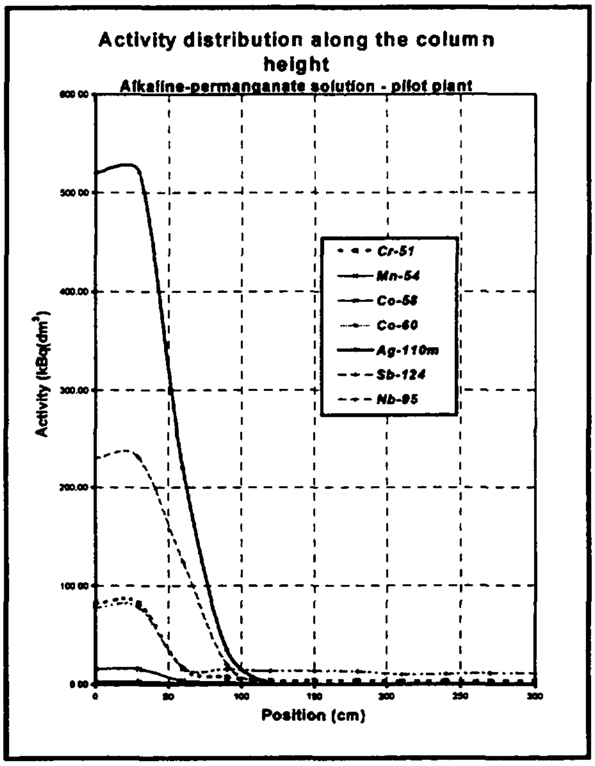
Time	Activity concentration in the outlet oxidising solution (kBq/dm^3)								
	^{51}Cr	^{54}Mn	^{58}Co	^{60}Co	^{110m}Ag	^{124}Sb	^{95}Nb	$\sum^{54}$Mn, ^{60}Co, ^{110m}Ag	Total
Feed solution	82	15.4	2.9	1.6	520	77.7	230	537	929.6
24	0.22	0.08	0.04	0.24	0.26	1.02	0.04	0.58	1.9
57	0.40	0.16	0.1	0.36	0.38	1.94	0.12	0.90	3.46
77	0.56	0.08	0.06	0.16	0.52	4.80	0.12	0.76	6.3
93	0.58	0.06	0.06	0.14	0.16	5.40	0.08	0.36	6.48
113	1.16	0.02	0.06	0.12	0.10	6.78	0.06	0.24	8.3
136	1.76	0.08	0.08	0.22	0.28	8.06	0.08	0.58	10.56
152	3.56	0.16	0.24	0.22	0.30	10.46	0.44	0.68	15.38
173	3.24	0.14	0.22	0.24	0.16	10.74	0.36	0.54	15.1

Table 6b: Decontamination waste treatment tests with layered ion exchange sorption system

Time	Activity concentration in the outlet decontaminating solution (kBq/dm^3)								
	^{51}Cr	^{54}Mn	^{58}Co	^{60}Co	^{110m}Ag	^{124}Sb	^{95}Nb	$\sum^{54}$Mn, ^{60}Co, ^{110m}Ag	Total
Feed solution	32	280	280	940	107.6	14.5	46.8	1327.6	1700.9
18	3.26	0.18	0.26	0.39	0.32	0.66	0.43	0.76	5.5
38	1.36	0.06	0.08	0.10	0.10	9.20	0.08	0.26	10.98
55	4.46	0.18	0.26	0.34	0.44	15.40	0.50	0.96	21.58
73	1.88	0.04	0.08	0.08	0.08	13.10	0.10	0.20	15.36
89	4.48	0.18	0.32	0.36	0.30	15.30	0.56	0.84	21.5
106	5.10	0.22	0.34	0.36	0.40	14.70	0.54	0.98	21.66
126	6.70	0.22	0.40	0.40	0.30	15.90	0.90	0.92	24.82



6. Figure: Ion exchange sorption tests (2)



7. Figure: Ion exchange sorption tests (1)

In the test with the alkaline-permanganate solution the ion exchanger-sorption column was filled with activated carbon (Top-Sorb) in 180 cm of column height. The bottom part of the column (300 * 5.5 cm I.D.) was filled with cation exchanger resin in the Fe^{2+} form and H$^+$ (40-40 cm layer height and d$_p$: 0.4-1.2 cm). A 40 cm layer of anion exchanger resin in OH$^-$ form was placed on the bottom of the column. In test with citric acid-oxalic acid solution the activated carbon layer height of column (150 * 5.5 cm I.D.) was only 30 cm. In this case the middle part of column (80 cm layer height) was filled with H$^+$ cation exchanger resin. This column contains in the bottom part 40 cm height anion exchanger layer as well.

From the diagrams it can be stated that the main working layer of the bed was the specially pre-treated activated carbon layer. In case of the alkaline-permanganate solution the reactive adsorption of MnO_2 precipitate is the main factor that has important role in the further adsorption or co-precipitation of other radioactive specimens.

The experimental modelling results show that under the above mentioned circumstances ^{54}Mn, ^{60}Co, ^{58}Co, ^{95}Nb and ^{110m}Ag has great affinity to the activated carbon adsorbent. The reduction processes of Mn(VI) and Mn(VI) have significant role.

During the test it was stated that during the treatment of alkaline solution the activity removal is dependent on a multi-step reactive adsorption process. The following transport steps occur on activated carbon sorbent if we consider a solution contains the alkaline permanganate, sodium hydroxide and Ag ions:

1. External diffusion of Mn(VII) and Ag ions in Nernst layer,
2. Internal diffusion of Mn(VII) and Ag ions in pores;
3. Mn(VII) reduction to Mn(VI) reaction on the surface of activated carbon (CO_2 dissolves in the alkaline solution);
4. Disproportionation of Mn(VI) in the pores, precipitation of the MnO_2 in the pores;
5. Adsorption of Ag ions (model ions);

Avoiding the further detailed description of the process results we have stated the followings (the batch process was used as test method):

- The rate of redox process (3) is dependent on the temperature and quantity of sorbent. If the temperature and the amount of sorbent increase, the rate of the process increases as well. Rate constant was analysed.
- The disproportionation process is dependent on only the temperature.
- Silver adsorbs on the carbon as colloid particulate.
- On the base of the experiments with real solutions we think that similar phenomena valid for other nuclides.
- In the acidic solutions the phenomena is not so clear, the activated carbon with layer of MnO_2 precipitate is also suitable for activity removal in combination with pre-treated ion exchanger layer.

Qualification of a full system decontamination technology

In 1996 we have started a qualification programme for the implementation of full system decontamination technology. We took into account the some experiences from decontamination of Loviisa No. 2 units primary system in this phase.

During the pre-qualification work we have done the followings:

- The system to be decontaminated was outlined;
- The system parameters to be controlled during the decontamination were outlined (temperature, pressure, concentrations and so on).
- A document with the summary of research results (oxidation, decontamination, corrosion, waste treatments, other connected investigations) and international results in the field of the full system decontamination was prepared to clear the present state of the project.
- A preliminary qualification programme has been prepared.
- The preliminary version of structural materials balance and the related plan of the corrosion tests documents have been prepared.
- A first version of a decontamination technology that is proposed to be used as full system decontamination was outlined. It includes the following main steps:
    - Oxidation of the corrosion layer;
    - Removal of the oxidising agent a precipitate traces from primary surfaces;
    - Decontamination with a low concentration reductive solution;
    - System flushing;
    - Passivation of primary surfaces.
- Some of the preliminary corrosion test with CITROX, alkaline-permanganate and acidic permanganate oxidation, and V(II)-C(II)-gluconic acid and EDTA system have been carried out.

It was proposed that the useful waste treatment procedures are ion exchange and sorption in combination with chemical or electrochemical degradation of complexing chemicals.

In the next step of the qualification programme the plant personnel at Paks NPP should revise and, after further completion, approve these documents.

The preliminary corrosion test measurements were carried out in connection with the previously described decontamination and oxidation tests.

We have measured the corrosion effects of the solutions used on 08H18N10T-type stainless steel. We have used a flow-through polarisation cell to get polarisation curves in solutions. The flow rate of solution was 800 cm^3/min, the temperature of the measurement was 95°C.

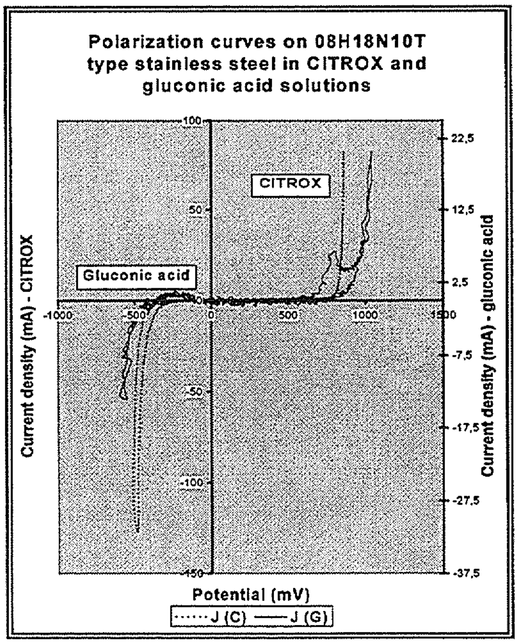
The polarisation curves are presented on the Figure No 8 and 9. The parameters of the curves are summarised by the following table.

Table7: Summary of evaluation data of the polarisation curves

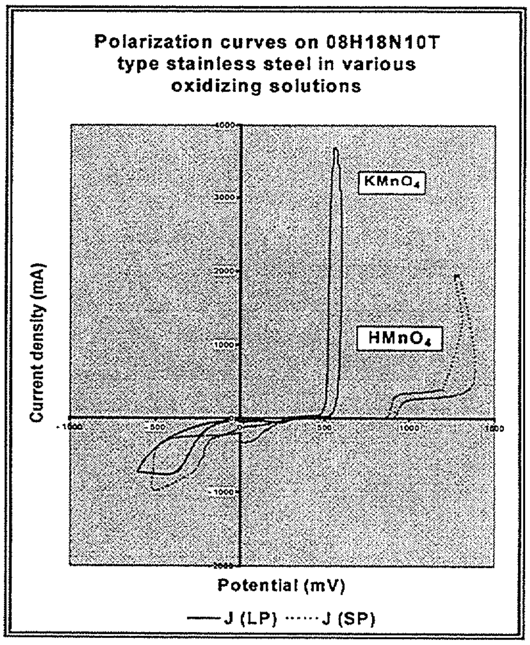
Solution	$E_{(j=0)}$ MV	R_k mΩm^2	$1/R_k$ 1/mΩm^2	**H** mV	E_k mV	log j_0	j_0 A/m^2
CITROX	-141	1000	0.001	830	-90	-1.46	0.035
Gluconic acid	567	303.03	0.0033	680	140	-3.22	0.0006
$HMnO_4$	783	95.23	0.0105	920	730	-0.30	0.50
$KMno_4$	219	4.34	0.230	580	205	0.05	4.46

Comment:

$E_{(j=0)}$	current free potential
R_k	corrosion resistance
η	over-potential
E_k	corrosion potential
j_0	corrosion current density



8. Figure: Results of corrosion measurements with decontaminating solutions.



9. Figure: Results of corrosion measurements with oxidising solutions.

On the base of figures and data above can be stated that both the gluconic acid comparing to the CITROX and also permanganic acid comparing to the alkaline permanganate are less corrosive. In permanganic acid solution the corrosion potential more positive (about 730 mV) than in alkaline permanganate (about (205 mV). If the phosphoric acid is added to the permanganic acid solution the corrosion potential increase to about 820 mV. The potential decrease in alkaline solution can be explained by forming of hydroxo-complexes. This phenomena decrease the potential and increase the rate of the corrosion (refer to j_0 and R_k). The corrosion current density in permanganic acid solution is smaller than in alkaline permanganate solution. The difference is about one order of magnitude.

In gluconic acid solution the corrosion potential more positive than in CITROX solution (-90 mV and 140 mV respectively). We have also done comparative test with CITROX solution, high concentration oxalic acid solution and solutions with nitric acid. We have stated that the main corrosion agent is the oxalic acid in the CITROX solutions. The degree of the corrosion increases with the concentration of oxalic acid. In the case of the nitric acid containing solutions significant corrosion can occur at low nitric acid concentration as well.

In the gluconic acid and permanganic acid at certain polarisation potential a passivation of samples are indicated on the observed polarisation curves.

We have planed to investigate the corrosion effect of the solutions in more detail together with corrosion testing of the reducing decontaminating solutions as well.

Summary and conclusions

To summarise our results we can claim that we managed to overcome two significant problems of the reagent system used; namely the sulphate content and the radiolysis of the applied complexing agent. Although this brings about some slight sacrificing of efficiency, it is still worth it especially if we take the significantly lower energy consumption into consideration (55°C instead of 90°C).

It is very important, though that the pre-treatments (oxidising and acidifying steps) are complete otherwise the reagents - V(II) and Cr(II) - can be consumed in a side reaction with water catalysed by residual mixed metal-oxides. While Cr(II) does not do the reduction itself, if added to V(II) containing solution it shows a synergistic effect accelerating considerably the decontamination process.

From the results of oxidation test we can state that the oxidation with permanganic acid is suitable pre-treatment method for oxidising the corrosion layers, with lover chemicals content and/or shorter period of treatment time.

The generation of MnO_2 precipitate cannot be avoided by using of permanganic acid stabilised with phosphoric acid. But on the base of our experiments it is clear that any tested solution is suitable for the effective removal of the precipitate.

Because oxalic acid can initiate inter-granular stress corrosion, mainly on welded specimens, it is recommended to use gluconic acid for removing the MnO_2 precipitate and as complexing agent in decontaminating step. The corrosion effects of the treatments shall be investigated in more details before practical use. On the base of detailed experiments with V(II)-Cr(II) containing solutions with gluconic acid complexant it is stated that the washing step for removing the MnO_2 precipitate and the reducing treatment for dissolution of corrosion layer can combine in one step with increased gluconic acid concentration in it.

We have also investigated the decomposition of the waste generated during the treatments. The gluconic acid content can be easily decomposed comparing to EDTA and other complexants.

The investigated ion exchange - adsorption system is useful for treatment of waste generated during the *oxidising and decontamination step. Further investigations are necessary to evaluate the system performance for* acidic oxidising solutions and for gluconic acid containing decontaminating solutions as well. Test system includes three layered cartridge columns is under implementation phase. The technical and implementation designs are completed. The system is now under the licensing phase.

In the next future we are going to continue the research programme and qualification a full system decontamination technology. In the frame of the continuing project the following task shall be carried out:

- Additional dissolution test using real samples taken from primary surfaces by the sampling system developed.
- Introducing permanganic acid and gluconic acid as decontamination chemicals.
- Evaluation and comparison of results gained to choose the right full system decontamination procedure.
- Process design and licensing by the nuclear regulatory body.
- Investigation and evaluation of passivation method used after full system decontamination.
- Implementation of liquid radioactive waste treatment system for decontamination solutions and complexing agents as well.

REFERENCES

1. J. Makai, J. Schunk, Zs. Szabó, I. Schremmer: Kinetics of magnetite dissolution using LOMI reagents
2. T. Szánya, L. Hanák, G. Simon, Gy. Marton, J. Argyelán, J. Makai, J. Schunk et all: Purification of Radioactive Decontamination Liquids from Nuclear Power Plant Paks with Adsorption and Ion Exchange
3. G. Simon, T. Szánya, L. Hanák, Gy. Marton, J. Hideg J. Makai, J. Schunk, P. Tilky: Purification of Nuclear Power Plant Decontamination Solution by Preparative Scale Reactive Adsorption
4. J. Makai; P. Komáromi; A. Krójer; J. Kreisz; I. Schremmer (G.I.C. Ltd.) J. Schunk (Paks NPP): Development of the full system decontamination technology at Paks NPP; Alternative oxidation of the primary corrosion layer

XA9847488

LABORATORY AND LOOP STUDIES ON CHEMICAL METHODOLOGIES FOR DECONTAMINATION OF BWR COOLANT SYSTEM SURFACES

P.N. MOORTHY, S.V. NARASIMHAN, J.L. GOSWAMI,
S. RANGARAJAN, S DUTTA
Bhabha Atomic Research Centre,
Trombay, Mumbai,
India

Abstract

Laboratory powder dissolution studies have been carried out on moderately sintered α-Fe_2O_3 (haematite) in citric acid - EDTA - ascorbic acid (CEA) mixtures of different compositions to identify the role of each component and arrive at an optimum composition to effect fast and quantitative dissolution. Experiments involving other reducing agents (in place of ascorbic acid) and chelating agents (in place of EDTA) revealed that there are no better substitutes for these two reagents. Samples prepared by heating ferrous hydroxide at different temperatures from 373 - 1073 K exhibited vastly different dissolution behaviour. Chromium substituted iron oxides prepared by heating the coprecipitated mixture of the two hydroxides at high temperature in the required proportions were having low solubility in the CEA mixtures. Pretreatment of these by alkaline permanganate (AP) rendered them somewhat more soluble, particularly in CEA mixtures containing higher ascorbic acid concentrations. Comparative evaluation of the efficacy of single and multi-step AP-CEA and AP-LOMI processes has been made by carrying out experiments on decontamination of contaminated specimens of oxide coated SS-304 surfaces from the reactor water clean-up circuit piping of Tarapur Atomic Power Station (TAPS) BWRs both in once through and closed loop circulation modes. A methology has been worked out for compaction of the radwastes arising from chemical decontaminations employing AP-CEA and AP-LOMI processes - this involves simply mixing of the AP and CEA or LOMI effluents in proper proportions and digesting at 363 K when MnO_2 precipitates out carrying with it more than 99% of the radioactivity.

1 INTRODUCTION

In all types of water cooled nuclear power reactors viz. BWRs, PWRs and PHWRs corrosion products which are generated as a result of structural material - primary coolant interactions get transported to the core where they can deposit on the fuel surfaces and become activated by neutron irradiation. The activated corrosion products are released back into the circulating coolant and eventually get deposited on the out - of - core surfaces resulting in build up of radiation fields in areas where personnel access is required for maintenance and servicing. Over a period of time this results in relatively high occupational doses which must be controlled to ensure compliance with statutory requirements.

There are many possible ways of reducing the radiation doses received by personnel in nuclear power plants such as improvement in reactor design in terms of choice of proper materials of construction and operation with improved coolant chemistries which are conducive to minimising in-core deposition of corrosion products. But in recent years chemical decontamination methodology which involves the dissolution of radioactive deposits from the surfaces of structural materials in the primary coolant circuit without causing undue corrosion to the base metal has evolved as a practical solution to the problem of high radiation fields on out-of-core surfaces.

The radionuclides in the system get incorporated in the oxide layers on the inner side of pipework and components. These oxides are complex in composition and vary between reactor types and also between different surfaces even in the same reactor depending on the materials of construction, coolant pH, dissolved oxygen concentration and temperature. In all the above reactor types iron bearing alloys are the main constructional materials in the primary coolant circuit. Hence oxide compositions ranging from haematite, nickel ferrite, magnetite, Ni and Cr substituted ferrites and the underlying iron chromite are observed on surfaces exposed to BWR coolant containing higher dissolved oxygen (thicker oxide layer) whereas in the PWR coolant under reducing chemistry conditions one observes magnetite, iron chromite and high chromium and nickel substituted ferrites (thinner oxide layer) [1]. In PHWR coolant circuits magnetite is the principal oxide deposit. Any chemical decontamination methodology has therefore to be addressed to dissolution of such oxides. A number of detailed laboratory studies on the dissolution of iron oxides and mixed oxides containing iron, nickel and chromium have been reported in the literature [2-17].

2 BACKGROUND AND OBJECTIVES OF THE RESEARCH PROJECT

Indian nuclear power programme comprises of two operating 200 MWe BWR units at Tarapur (TAPS) and two operating 220 MWe PHWR units each at Rawatbhatta (RAPS), Kalpakkam (MAPS), Narora (NAPS) and Kakrapara (KAPS). Concerned with the gradually increasing radiation fields on the out-of-core coolant surfaces (largely carbon steel) of the four earlier PHWR units, our group has developed the dilute chemical decontamination technology for these reactors and this was successfully employed in MAPS Unit #1 in Dec 1993, MAPS Unit #2 in April 1995 and again in MAPS Unit #1 in Nov 1997. The present project is aimed at developing a suitable methodology for the chemical decontamination of the primary coolant system surfaces (stainless steel) of the TAPS BWRs. The work under the project involved : (i) preparation of different types of iron oxides representative of reactor system surfaces ; (ii) study of their dissolution behaviour in different reagent systems ; (iii) decontamination experiments on specimen pieces cut from the primary coolant circuit piping of an operating BWR and (iv) experiments aimed at compaction of radioactive wastes arising from chemical decontamination.

3 TECHNICAL APPROACH

3.1 Preparation of different iron oxides

Ferrous hydroxide was precipitated from 1 mol m^{-3} $FeSO_4$ solution by adding 50% NaOH in an inert atmosphere and heated in air for 6 hrs at various temperatures ranging from 373 - 1073 K. After heat treatment the samples were characterised by chemical analysis and powder X-ray diffraction (XRD). It was found that crystalline α-Fe_2O_3 (haematite) was formed on heat treatment at temperatures $>$ 773 K. The sample heated at 673 K showed less developed peaks of α-Fe_2O_3 . At lower temperatures the samples were less crystalline in nature and from their powder XRD patterns they were identified as defect inverse spinel oxides. The oxide prepared by heating ferrous hydroxide at 873 K for 6 hrs is referred to as ‘ moderately sintered haematite ’. For preparing Cr-substituted haematites, the Fe(II) and Cr(III) ions corresponding to different initial ratios were coprecipitated as hydroxides at room temperature under inert atmosphere and the precipitate was digested for 6 hrs on a steam bath also under inert atmosphere. From the Differential Thermal analysis (DTA) studies of these coprecipitated hydroxides in air the temperature corresponding to the formation of the single phase oxides was determined to be 1073 K. The coprecipitated hydroxides were then heated in air for 4 hrs at this temperature. The oxides, thus prepared gave sharp and symmetric XRD peaks confirming the presence of single phase species.

3.2 Powder dissolution studies

The dissolution experiments on oxide powders prepared as above were performed in a magnetically stirred cylindrical glass vessel provided with a thermostatic water jacket (Fig. 1). 200 cm^3 of the dissolution mixture with the required concentration of the components (viz. citric acid, EDTA and ascorbic acid - refereed to as CEA) was deareated for 60 min by purging with argon. Oxide powders of weight corresponding to 22 mol m^{-3} Fe were used for the dissolution experiments. This quantity of oxide corresponds to dissolving a coating thickness of about 5 microns of oxide in a system having surface area/volume ration of 67 m^{-1} taken in a solution volume of 200 cm^3. The initial pH was adjusted to 2.8 with nitric acid. Experiments were performed under inert atmosphere by keeping a steady flow of oxygen-free argon gas through the mixture throughout the duration of the experiment. Samples were periodically withdrawn, centrifuged and filtered through 0.2 μm pore size membrane filter. Iron concentrations in the filtrate were determined spectrophotometrically by the standard o-phenanthroline method and Cr content was analysed by AAS. Treatment with alkaline permanganate ($KMnO_4$ in NaOH) was also carried out in the same apparatus, but without inert gas purging.

3.3 Coupon decontamination experiments

Test coupons of dimensions 26 mm x 26 mm x 6 mm thick cut from a section of the 100 mm OD SS-304 piping removed from the reactor water clean-up system circuit of TAPS Unit #1 were used in the experiments. These coupons had oxide coating of approx. 2 μm thickness on the curved inner surface which had been exposed to the BWR coolant environment (553 K, 70 Kg/cm^2, pH 6.2, DO 200 ppb) over about 20 years of operation and their radioactivity content was ~ 7 μCi cm^{-2}, the surface dose rate being ~ 1000 mR/hr. The solutions (volume ~ 600 cm^3) with which these were treated at ~340 K for 4-5 hrs either singly or sequentially one after the other are : (i) AP (alkaline permanganate) - 0.3% $KMnO_4$ in 1.5% NaOH, (ii) CE - 1% citric acid and 0.3% Na_2EDTA and (iii) CEA - 2 mol m^{-3} with respect to each of citric acid, EDTA and ascorbic acid adjusted to pH 2.8 and (iv) LOMI - 4 mol m^{-3} in $V(HCO_2)_2$, 13 mol m^{-3} in HCOOH and 24 mol m^{-3} in picolinic acid. The treatment was carried out by suspending the coupons in the appropriate solution in a glass flask with arrangement for purging with inert gas to make the solutions oxygen-free and maintain an inert atmosphere (this was done only in the case of treatments with CEA

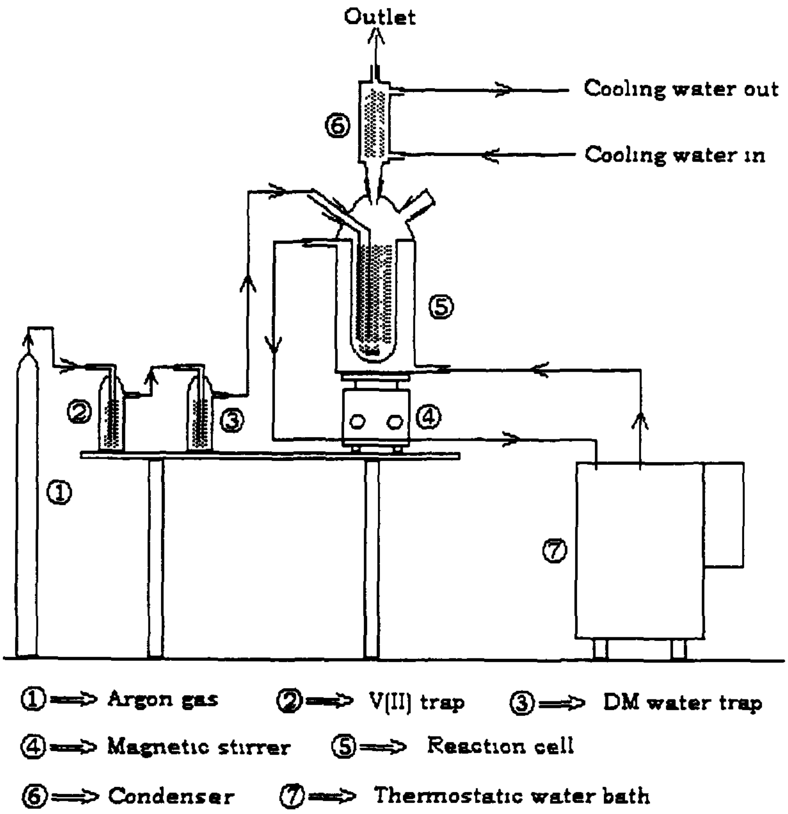


Fig. 1 : **Experimental set up for powder dissolution experiments**

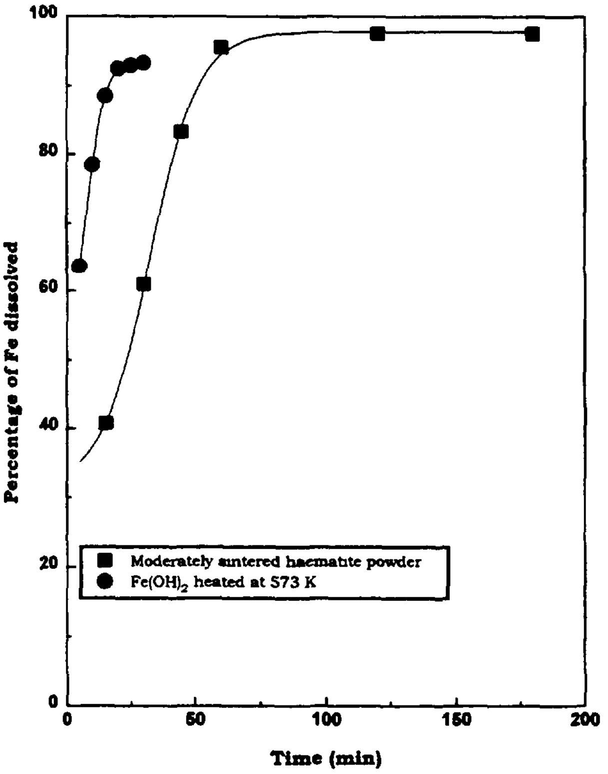


Fig. 2 : Typical plots of dissolution of iron oxides in CEA 11:44:4 mol m^{-3} mixture at 353 K

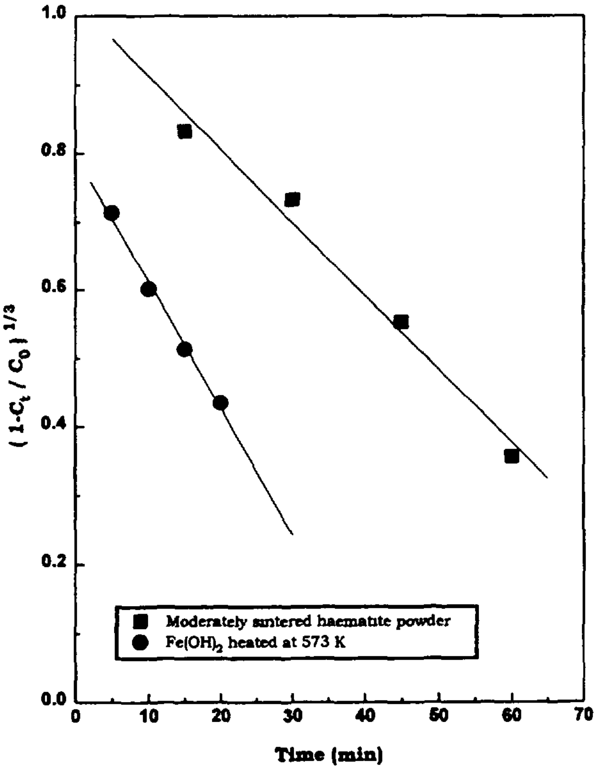


Fig. 3 : Typical inverse cubic rate law plots for dissolution of iron oxides in CEA 11:44:4 mol m^{-3} mixture at 353 K

and LOMI solutions). Solution analyses for Fe and Cr were carried out as described in section 3.2. Standard methods were employed for measurement of solution radioactivity and radiation fields on specimen surfaces.

3.4 Loop experiments with spool piece

The loop experimental set up is shown in Fig. 4. This consisted of SS-304 spool pieces of dimensions 500 mm long x 100 mm NB cut from the reactor water clean-up system of TAPS-BWR (the same from which coupons were cut for experiments described in section 3.3) and, SS-304 solution preparation and circulation tanks connected as shown with circulating pump, valves, joints etc. using flexible tubing. The contents of solution preparation and circulation tanks could be purged with inert gas in the case of experiments with LOMI and CEA reagents. The entire system was maintained at 343 K employing external electrical heating. The dissolution reagents

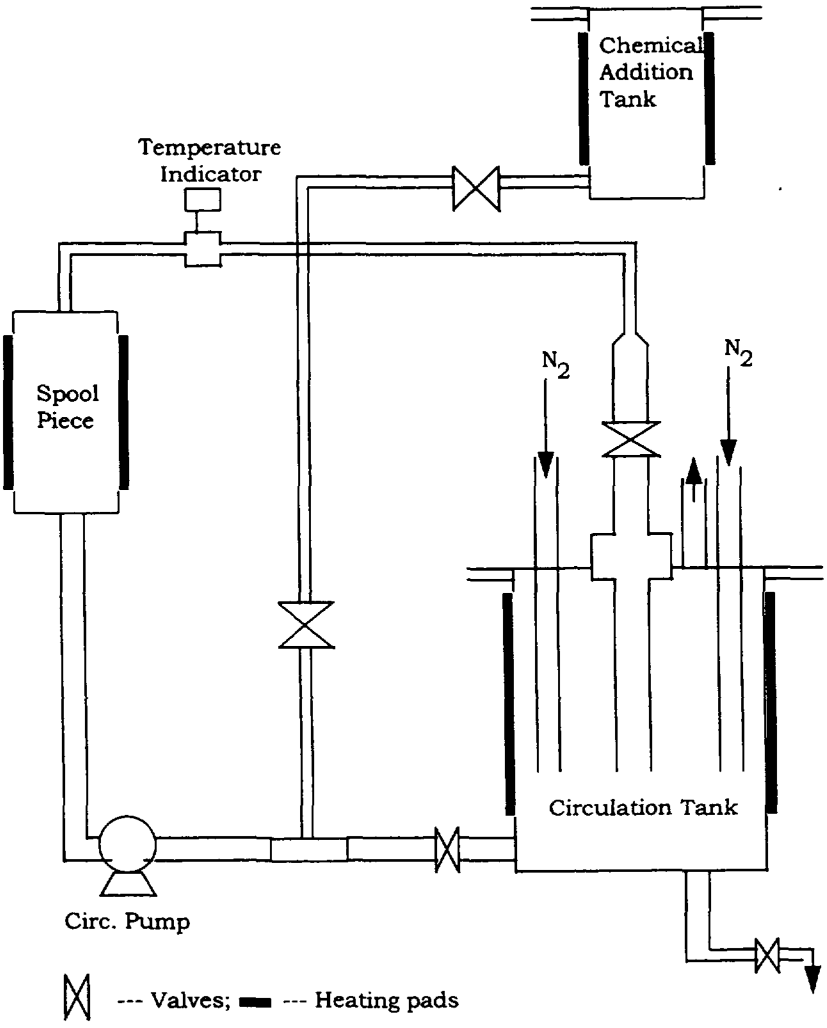


Fig. 4 : Schematic diagram of spool piece decontamination loop

used were the same as described in section 3.3. Solution analyses for Fe and Cr, and radioactivity and radiation field measurements were as described in section 3.3.

4 ACCOMPLISHMENTS

Typical plot of iron released as a function of time for the dissolution of moderately sintered haematite in 11:44:4 mol m^{-3} CEA mixture is given in Fig. 2, from which it is seen that there is rapid initial dissolution, the rate falling off with time and reaching a plateau (saturation) due to decrease in surface area of the particles as inferred by earlier workers [13,17]. This trend would suggest that the reaction occurs at the surface of the particles and the rate is proportional to the instantaneous surface area. The dissolution data were analysed according to the ' grain model ' proposed by Segal et al.[17] :$(1-C_t/C_0)^{1/3} = 1 - k_{obs}\, t$, where k_{obs} (dissolution rate constant) is given by : $k/r.\rho$, C_t and C_0 being the respective instantaneous and final concentrations of metal ion released, and ' r ' and ' ρ ' the particle radius and density respectively. Figure 3 illustrates representative inverse cubic rate law plots. The slope of the initial linear region of such plots gives k_{obs} . Linearity was observed upto about 75% dissolution in all cases.

Citric acid and EDTA individually were unable to dissolve moderately sintered haematite even when present in stiochiometrically excess concentration with respect to the oxide. Dissolution data in different CEA mixtures are summarised in Table 1. There was no appreciable increase in the maximum percentage dissolution with increase in citric acid concentration (11 mol m^{-3} - 66 mol m^{-3}), when the concentrations of EDTA and ascorbic acid were maintained constant at 2 and 4 mol m^{-3} respectively, whereas the dissolution rate constant increased upto 33 mol m^{-3} citric acid concentration beyond which it decreased. The decrease may be due to the formation of less soluble iron-citrate complex and also adsorption of citric acid on active sites on the oxide. In presence of stoichiometric/excess of EDTA and minimum concentration of ascorbic acid, citric acid initially enhanced the dissolution rate due to the availability of additional H^+ ions which contribute to the acid assisted dissolution route. Citric acid also helps to control the pH during the dissolution process (Table 2). Since adsorption of ligands is maximum at pH 2-3, it is preferable to maintain almost a constant pH of ~ 3 throughout the dissolution period. As seen in Table 2 if the initial pH is not adjusted to 2.8 the dissolution rate constant decreases leading to lesser percentage dissolution. The role of citric acid in controlling the pH becomes more important at lower EDTA concentrations where the pH changes are more pronounced.

TABLE 1 : Dissolution of moderately sintered haematite at 80^0 C in different CEA mixtures

Mixture concentration (mol m^{-3})			Percentage dissolution in 4 hrs	Time for complete dissolution	Dissolution rate constant k_{obs} x 10^3 (min^{-1})
C	E	A			
Citric acid variation					
11	02	04	36	> 8 hrs (43%)	1.3
22	02	04	39	> 8 hrs (47%)	1.5
33	02	04	37	> 8 hrs (41%)	2.2
44	02	04	49	> 8 hrs (54%)	2.2
55	02	04	42	> 8 hrs (51%)	1.7
66	02	04	43	> 8 hrs (55%)	1.4
00	22	04	89	6 hrs	5.2
02	22	04	97	3-4 hrs	5.8
11	22	04	92	3-4 hrs	8.0
22	22	04	93	3-4 hrs	4.2
00	44	04	96	3-4 hrs	5.7
11	44	04	97	3-4 hrs	9.9
EDTA variation					
02	00	04	06	> 8 hrs (09%)	1.6
02	11	04	54	> 8 hrs (56%)	4.0
02	22	04	97	3-4 hrs	5.8
02	33	04	95	3-4 hrs	6.3
02	44	04	95	3-4 hrs	7.3
02	55	04	96	3-4 hrs	9.0
Ascorbic acid variation					
00	00	80	18	> 8 hrs (28%)	1.2
02	02	04	18	> 8 hrs (20%)	1.9
02	02	10	22	> 8 hrs (28%)	2.0
02	02	25	29	> 8 hrs (34%)	1.7
02	02	40	36	> 8 hrs (44%)	1.7
02	02	60	45	> 8 hrs (57%)	1.7
02	02	80	54	> 8 hrs (68%)	1.6

(C : Citric acid ; E : EDTA ; A : Ascorbic acid)

Although stoichiometrically excess EDTA alone was unable to bring about any dissolution, it was very effective in presence of ascorbic acid. Complete dissolution was observed in 3-4 hrs in the presence of minimum amount of ascorbic acid. On varying EDTA concentration in the presence of 2 mol m^{-3} citric acid and 4 mol m^{-3} ascorbic acid, the dissolution rate increased linearly as the concentration of EDTA was increased (Table 1). There was no dissolution in mixtures containing only citric acid and EDTA. With varying ascorbic acid concentration at constant citric acid and EDTA concentrations (2 mol m^{-3}), the percentage dissolution in 4 hrs increased from 18-54%. In presence of stoichiometric or excess EDTA with respect to Fe, minimal concentrations of citric and ascorbic acids were sufficient to bring about rapid dissolution. Ascorbic acid acts as an initiator for the dissolution process by initially reducing the lattice Fe(III) ions to Fe(II) ions which are then released into solution by complexation with EDTA. The Fe(II)-EDTA complex being a good reducing agent accelerates the dissolution.

TABLE 2 : pH variation in the dissolution of moderately sintered haematite in different CEA mixtures at 80^{0}C.

Mixture concentration (mol m^{-3})			pH		Dissolution rate constant k_{obs} x 10^3 (min^{-1})	Time for complete dissolution
C	E	A	Initial	Final		
00	22	04	2.8	4.7	5.2	6 hrs
02	22	04	2.8	4.1	5.8	3-4 hrs
11	22	04	2.8	3.6	8.0	3-4 hrs
00	44	04	2.8	4.0	5.7	3-4 hrs
02	44	04	2.8	3.3	7.3	3-4 hrs
11	44	04	2.8	3.15	9.9	3-4 hrs
02	55	04	2.8	3.0	9.0	3-4 hrs
11	44	04*	3.1	3.8	8.5	3-4 hrs
02	55	04*	3.3	5.2	3.8	> 4 hrs (67%)

(C : Citric acid ; E : EDTA ; A : Ascorbic acid)

* Initial pH of the mixture not adjusted to 2.8

TABLE 3 : Dissolution of moderately sintered haematite in 11:44:4 mol m^{-3} CEA mixture at different initial pHs.

pH	Percentage dissolution in 4 hrs
6.0	24
5.0	43
4.0	67
3.0	100
2.0	Complete dissolution in 2-3 hrs#
1.0	Complete dissolution in 2-3 hrs#

EDTA precipitation occurs

In order to find out the effect of pH on the dissolution, experiments were performed in 11:44:4 mol m^{-3} CEA mixture at different initial pHs from 1 - 6. From the results (Table 3) it is seen that a very rapid dissolution occurs at low pHs, whereas above pH 3.0 dissolution is appreciably slower. The faster dissolution at lower pHs is due to contribution of the acid assisted dissolution of the oxide.

From the results of studies using different reducing agents in solutions containing 11 mol m^{-3} citric acid and 44 mol m^{-3} EDTA (Table 4) it is seen that the dissolution of moderately sintered haematite is very fast, complete dissolution occurring in 3-4 hrs when ascorbic acid is used as the reducing agent. In the case of thioglycolic acid as the reductant it is ~ 49% and with hydrazine <4%, and no dissolution at all was observed in 4 hrs when sodium dithionite, oxalic acid and formic acid were used as reductants. It is obvious that there is no corelation between the extent of dissolution and reduction potential, and other factors such as adsorption of the reductant on the oxide surface which is also pH dependent may also have to be taken into account.

Dissolution data for different chelating ligands in solutions containing 11 mol m^{-3} citric acid and 4 mol m^{-3} ascorbic acid along with the stability constants of the Fe(II) complexes formed with these ligands are given in Table 5. Complete dissolution occurs in 4 hrs when EDTA and DTPA are used as the chelating ligands, whereas in the case of HEDTA and NTA it is ~ 79% and ~ 39% respectively. In the case of IDA there is practically no dissolution in the initial stages but there is ~ 22% dissolution in 4 hrs. Fe(II)-DTPA and Fe(II)-EDTA complexes have very high stability constants and this makes them strong reductants capable of accelerating the dissolution process. Stability constants of complexes of Fe(II) with other ligands are much lower and these are ineffective in dissolving α-Fe_2O_3 at appreciable rate. The data in Table 5 reflect these trends.

Dissolution behaviour of iron oxides prepared by heating $Fe(OH)_2$ in air at different temperatures are given in Table 6. Complete dissolution in 3-4 hrs was observed in the case of samples heated at 773 K and above. The samples heated at 673 K dissolved completely in 2 hrs and in the case of those heated at 573, 473 and 373 K, the dissolution was very rapid with complete dissolution occurring in less than 30 mins. Samples heated at low temperatures are less crystalline in nature as compared to those heated at higher temperatures. The ferrous hydroxide precipitated

TABLE 4 : Effect of different reducing agents on the dissolution of moderately sintered haematite in citric acid - EDTA mixtures at 80°C

Reducing agent (4 mol m^{-3})	Redox potential E^0 (vs NHE)	Percentage dissolution in 4 hrs.	$k_{obs} \times 10^3$ (min^{-1})
Ascorbic acid	+0.412 V	100	9.9
Thioglycolic acid	-0.23 V	49	2.3
Hydrazine	-1.15 V	<4	-
Sodium dithionite	-0.40 V	No dissolution	-
Oxalic acid	-0.23 V	No dissolution	-
Formic acid	-0.056 V	No dissolution	-

*(Citric acid 11 mol m^{-3}; EDTA 44 mol m^{-3})

TABLE 5 : Effect of different complexing agents on the dissolution of moderately sintered haematite in citric acid - ascorbic acid mixtures at 80°C.

Chelating agents (44 mol m^{-3})	Log K	Percentage dissolution in 4 hours	$k_{obs} \times 10^3$ (min^{-1})
DTPA	16.4	100	6.2
EDTA	14.3	100	9.9
HEDTA	12.2	79	5.2
Oxalic acid	9.4	59	2.1
NTA	8.3	39	1.2
IDA	5.8	22	0.3

(Citric acid 11 mol m^{-3}; Ascorbic acid 4 mol m^{-3})

TABLE 6 : Dissolution behaviour of iron oxides* in CEA 11:44:4 mol m^{-3} mixture at 80°C

Temperature (K) of heat treatment	$k_{obs} \times 10^3$ (min^{-1})	Time for complete dissolution
373	46.7	< 30 mins
473	31.2	< 30 mins
573	20.0	< 30 mins
673	12.5	2 hrs
773	10.3	3-4 hrs
873	09.9	3-4 hrs
1073	06.6	3-4 hrs

* Prepared by heating $Fe(OH)_2$ in air at different temperatures for 6 hrs.

at ambient temperature has a porous structure, and on heating at low temperatures these pores may not coalesce to any significant extent to form a compact phase. This in turn will cause weaker binding between the crystallites thus facilitating better access to the solution mixture and hence faster dissolution. Increase in treatment temperature renders stronger binding between the crystallites and increases the crystallinity (less porosity) of the sample prepared by heating at 1073 K. In highly crystalline samples the compact nature of the lattice hinders the reduction of the lattice Fe(III) ions by the reducing agent and hence the release of the reduced Fe(II) ions into the solution by complexation with the chelating agent would be rather slow.

α-Fe_2O_3 prepared by heating $Fe(OH)_2$ at 1073 K showed near identical dissolution behaviour as the moderately sintered sample prepared at 873 K. The chromium substituted oxides prepared by heating at 1073 K, were more difficult to dissolve in CEA mixture as compared to α-Fe_2O_3 prepared at 1073 K (Table 7) suggesting that replacement of part of Fe(III) ions by Cr(III) ions in the spinel lattice increases the stabilization of the lattice, thereby hindering dissolution. It has been reported [1] that in the case of oxides especially spinels and inverse spinels containing chromium, an oxidative pre-treatment using alkaline permanganate (AP) is required to solubilise the Cr as CrO_4^{-2}, after which the chromium depleted iron oxides can be readily dissolved in a reductive - complexing formulation. However it was observed that when the Cr substituted haematites prepared by heating at 1073 K were treated with 0.3 -1% $KMnO_4$ in 1.2% NaOH at 353 K, chromium was not appreciably released from the oxides. On the other hand simple Cr_2O_3 prepared under the same conditions dissolved completely in this medium. It would appear that the hexagonal lattice of Cr substituted haematites has a high degree of lattice stabilization which makes the oxidation of Cr(III) in the host lattice very difficult. Such chromium substituted haematites also do not readily dissolve in any of the CEA mixtures.

In the case of low chromium containing haematite sample (3.5%) complete dissolution in CEA mixture was observed only at higher concentrations of the reducing agent (Table 7), the mechanism being reductive - complexation of Fe as in the case of unsubstituted haematites and simple complexation of Cr. When the low chromium containing oxide was first treated with 0.3% $KMnO_4$ in 1.2% NaOH there was no significant amount of chromium or iron released on subsequent treatment with 11:44:4 mol m^{-3} CEA mixture, but when $KMnO_4$ concentration was increased to 0.6%, there was considerable dissolution in this CEA mixture. Even at higher $KMnO_4$ concentrations only a fraction of the Cr(III) present in the lattice seems to get oxidised.

TABLE 7 : Dissolution behaviour of chromium substituted spinel oxides in different CEA mixtures and the effect of alkaline permanganate pre-treatment

Sample	Fe %	Cr %	Treatment	Percentage Dissolved*	
				Fe	Cr
$Fe_{1.93}Cr_{0.07}O_3$	96.5	3.5	CEA 11:44:4 mol m^{-3}	ND	ND
$Fe_{1.93}Cr_{0.07}O_3$	96.5	3.5	AP (0.3%$KMnO_4$ + 1.2% NaOH)	ND	L
			CEA 11:44:4 mol m^{-3}	ND	ND
$Fe_{1.93}Cr_{0.07}O_3$	96.5	3.5	AP (0.6%$KMnO_4$ + 1.2% NaOH)	ND	L
			CEA 11:44:4 mol m^{-3}	69	51
$Fe_{1.93}Cr_{0.07}O_3$	96.5	3.5	CEA 11:44:11 mol m^{-3}	70.5	61.5
$Fe_{1.93}Cr_{0.07}O_3$	96.5	3.5	AP (0.6%$KMnO_4$ + 1.2% NaOH)	ND	L
			CEA 11:44:11 mol m^{-3}	CD	CD
$Fe_{1.93}Cr_{0.07}O_3$	96.5	3.5	CEA 11:44:22 mol m^{-3}	CD	CD
$Fe_{1.9}Cr_{0.1}O_3$	95	5.0	AP (0.6%$KMnO_4$ + 1.2% NaOH)	ND	L
			CEA 11:44:11 mol m^{-3}	12	5
$Fe_{1.9}Cr_{0.1}O_3$	95	5.0	AP (1%$KMnO_4$ + 1.2% NaOH)	ND	L
			CEA 11:44:11 mol m^{-3}	43	19.5
$Fe_{1.9}Cr_{0.1}O_3$	95	5.0	CEA 11:44:22 mol m^{-3}	66	23.5
$Fe_{1.9}Cr_{0.1}O_3$	95	5.0	AP (1%$KMnO_4$ + 1.2% NaOH)	ND	L
			CEA 11:44:22 mol m^{-3}	80	42
$Fe_{1.9}Cr_{0.1}O_3$	95	5.0	CEA 11:44:44 mol m^{-3}	80	44.5
$Fe_{1.85}Cr_{0.15}O_3$	92.5	7.5	CEA 11:44:44 mol m^{-3}	61	27.5
$Fe_{1.85}Cr_{0.15}O_3$	92.5	7.5	AP (1%$KMnO_4$ + 1.2% NaOH)	ND	L
			CEA 11:44:22 mol m^{-3}	58	51
$Fe_{1.8}Cr_{0.2}O_3$	90	10	CEA 11:44:44 mol m^{-3}	15	10.5
$Fe_{1.8}Cr_{0.2}O_3$	90	10	AP (1%$KMnO_4$ + 1.2% NaOH)	ND	L
			CEA 11:44:22 mol m^{-3}	31	19.5
$Fe_{1.75}Cr_{0.25}O_3$	87.5	12.5	AP (1%$KMnO_4$ + 1.2% NaOH)	ND	L
			CEA 11:44:22 mol m^{-3}	14	6
$Fe_{1.75}Cr_{0.25}O_3$	87.5	12.5	CEA 11:44:44 mol m^{-3}	ND	ND
$Fe_{1.75}Cr_{0.25}O_3$	87.5	12.5	AP (1%$KMnO_4$ + 1.2% NaOH)	ND	L
			CEA 11:44:44 mol m^{-3}	41.5	24.5

* In 8 hrs
L : Low dissolution (3-5%)
ND : No significant dissolution (i.e. < 2-3 ppm Fe or Cr in solution)
CD : Complete dissolution

This slight disturbance of the lattice could facilitate the access of the reducing agent to the Fe(III) ions in the lattice in the subsequent treatment with the reductive - complexing formulation. Thus though there is no appreciable release of chromium in the AP pre-treatment step, it plays a definite role in facilitating the dissolution in the CEA mixture.

As the chromium content of the oxide increases it tends to become hard and a progressively higher concentration of the reducing agent is required to bring about some dissolution. Here also pre-treatment with a higher concentration of $KMnO_4$

followed by treatment with the CEA mixture resulted in higher extent of dissolution as compared to what was observed in the absence of pre-treatment. When the chromium content is above 10%, treatment with CEA alone using even very high concentration of the reducing agent (11:44:44 mol m^{-3}) was ineffective indicating the high degree of lattice stabilization of the oxide. However when this oxide was pre-treated with 1% $KMnO_4$ in 1.2% NaOH and subsequently treated with 11:44:44 mol m^{-3} CEA formulation there was some dissolution. This behaviour of chromium substituted haematites is quite different from what has been reported in the literature in the case of chromium substituted ferrites [1].

The results of coupon decontamination experiments are given in Table 8. These were primarily aimed at comparative evaluation of CEA as a reductive - complexing solvent with the known LOMI reagent for the specimens from the BWR coolant system piping. Whereas either of these formulations by themselves were not able to effect any

Table 8 : Results of Coupon Decontamination Experiments

Treatment*	Step DF	Cumulative DF	
AP	1.4		-
AP-1	1.0	2.6	6.5
LOMI-1	2.6		
AP-2	1.2	2.5	
LOMI-2	2.1		
AP/CE	-	1.1	
AP/CEA-1	-	1.6	3.4
AP/CEA-2	-	2.2	

(* Solution compositions are given in text, p 5) decontamination of the specimens, on pre-treatment with alkaline permanganate there was appreciable decontamination in the subsequent treatment step with LOMI or CEA formulations - the DFs observed in the case of AP-LOMI being appreciably higher than in the AP-CEA case. In either case, the DF in the AP pre-treatment step was only marginal, the actual decontamination occurring in the subsequent LOMI or CEA step. It is also seen that citric acid - EDTA mixture with no reductant (ascorbic acid) present is not able to bring about any decontamination even after the preoxidation with AP. These observations are also supported by the results of spool piece decontamination experiments (Tables 9-10). There was appreciable Cr release only in the AP step, but not in the subsequent LOMI or CEA step. On the other hand large amounts of Fe and radioactivity release occurred in the latter step. The spool piece experiments conclusively showed that AP-LOMI procedure leads to higher DFs as compared to AP-CEA, at least at the low concentration of CEA mixture (2:2:4 mol

TABLE 9 : Metal and radioactivity release during 2-cycle AP-LOMI decontamination of spool piece

Time (hr)	Metal concentration in solution (mg/Kg) Filtrate			Gross radioactvity in solution (nci/ml)
	Fe	Ni	Cr	Filtrate
1st AP step				
1	0.30	0.20	1.27	0.23
2	0.27	0.14	1.56	0.06
3	0.33	0.20	1.68	0.06
4	0.30	0.20	1.90	0.07
1st LOMI step				
1	28.01	2.90	0.44	198
2	30.50	3.45	0.85	239
3	32.27	4.22	1.33	257
4	34.04	5.07	1.77	269
2nd AP step				
1	0.18	0.13	0.65	0.10
2	0.27	0.16	0.52	0.05
3	0.15	0.16	0.67	0.06
4	0.12	0.13	0.76	0.06
2nd LOMI step				
1	6.22	0.57	-	15.7
2	9.39	0.72	-	23.2
3	12.98	1.07	-	26.1
4	19.06	1.13	-	28.3

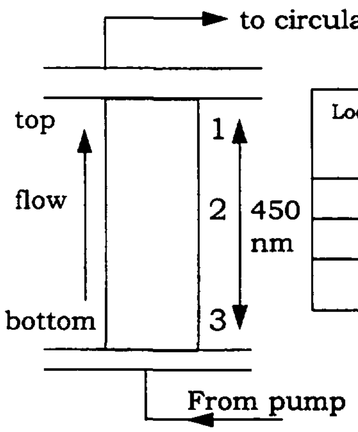
TABLE 10 : Metal and radioactivity release during 2-cycle AP-CEA decontamination of spool piece

Time (hr)	Metal concentration in solution (mg/Kg) Filtrate			Gross radioactvity in solution (nci/ml)
	Fe	Ni	Cr	Filtrate
1st AP step				
1	0.24	0.24	2.50	0.94
2	0.21	0.27	2.36	0.60
3	0.29	0.31	2.50	1.10
4	0.32	0.31	2.64	0.70
1st CEA step				
1	15.09	0.37	0.15	7.2
2	21.95	0.64	0.20	21.9
3	26.52	1.08	0.12	40.0
4	29.88	1.55	0.25	68.5
2nd AP step				
1	0.40	0.14	1.86	0.20
2	0.38	0.20	1.79	0.09
3	0.44	0.17	1.97	0.09
4	0.47	0.20	2.05	0.10
2nd CEA step				
1	4.24	0.24	0.10	8.2
2	6.17	0.41	0.12	17.8
3	17.36	0.72	0.10	35.9
4	23.53	1.10	0.15	55.2

m^{-3}) used in these experiments (Fig. 5). Use of such low concentrations was necessitated from the point of view of keeping the chemical contents in the waste effluents as low as possible. It was also observed during these experiments that although AP-LOMI procedure is superior from the point of giving higher DFs, in practical use it requires very stringent dissolved oxygen control during its preparation, storage and circulation, whereas CEA mixture is less sensitive to oxygen.

Although in decontamination campaigns it is the common practice to compact the radioactive waste solutions by use of ion exchangers, we have investigated an alternative possibility. Since the AP effluent is alkaline and contains a strong oxidant and the CEA or LOMI effluent (carrying the radioactive nuclides) is acidic and contains a strong reductant, mixing the two and digesting can be expected to bring

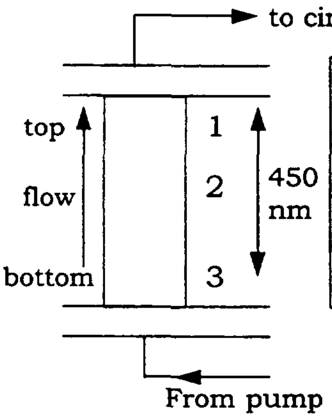
2-cycle AP-LOMI Process



Location	Field before decontamination (mR/h)	Field after decontamination (mR/h)	DF
1	700	20	35
2	900	17	53
3	900	25	36

Av. 41

2-cycle AP-CEA Process



Location	Field before decontamination (mR/h)	Field after decontamination (mR/h)	DF
1	900	100	9 0
2	950	200	4 5
3	800	400	2 0

Av. 5.2

Fig 5 : Results of two cycle AP-LOMI and AP-CEA decontamination of spool piece.

about their neutralisation and reduction of MnO_4^- to the Mn^{4+} stage and precipitation of the latter as MnO_2 which could trap the radioactive nuclides. Experiments in this direction showed that it is possible to trap more than 99% radioactivity in the MnO_2 precipitate when the two effluents are mixed in equal volumes and digested at ~ 90°C for 1 hr.

5 SUMMARY AND CONCLUSIONS

The overall conclusions of the present investigations are as follows :-

⇨ The dissolution of moderately sintered haematite in CEA mixtures involves ligand assisted reductive complexation process in which the different components have specific roles. Citric acid alone is not effective for the dissolution, but in presence of EDTA and ascorbic acid it aids the dissolution process. The role of ascorbic acid is to reduce the lattice Fe(III) ions to Fe(II) which are then complexed by EDTA thus solubilising the oxide.

⇨ Amongst the various reducing agents employed, ascorbic acid is the most effective one. EDTA and DTPA are the most effective chelating agents. The dissolution decreases at pHs above 3.0 whereas at pH ≤ 2.0 there is problem of EDTA precipitation although dissolution is not hampered.

⇨ Heat treatment of iron oxides significantly affects their dissolution in CEA mixtures - the higher the treatment temperature, the more difficult it is to solubilise the oxide.

⇨ Substitution of part of Fe(III) ions by Cr(III) ions in the haematite makes it more difficult to dissolve in the CEA mixture. When the chromium content is low (< 3.5%), complete dissolution is possible irrespective of whether or not an oxidative pre-treatment with alkaline $KMnO_4$ is carried out. The effectiveness of the dissolution of the oxides by the CEA mixture decreases as the chromium content of the oxides increases. Higher concentration of reducing agent or a pre-oxidation step with alkaline permanganate helps to some extent in dissolving high Cr containing oxides.

⇨ Both static and dynamic loop studies on specimen pieces cut from the Reactor Water Clean-up system piping of TAPS-BWR showed that a two cycle AP-LOMI process is capable of giving higher decontamination factors as compared to a two cycle AP-CEA process. However the former requires very stringent control on dissolved oxygen.

⇨ The radioactive LOMI or CEA effluents arising from decontamination using either the AP-LOMI or AP-CEA process can be mixed with the relatively inactive AP effluent and digested at ~ 90°C when MnO_2 precipitates out carrying with it all the radioactivity; this is envisaged as a simple way for radwaste disposal.

REFERENCES

[1] Swan, T., Segal, M.G., Williams, W.J., Pick, M.E., ' LOMI Decontamination Reagents and Related Preoxidation Processes ' in EPRI - NP 5522M (1987)

[2] Ayres, J.A., Decontamination of Nuclear Reactors and Equipments, Ronald Press Company NY (1970)

[3] Bradbury, D., ' The Chemical Dissolution of Fe(III) Oxides ' in Water Chemistry of Nuclear Reactor System,BNES 1, 373 (1977)

[4] Chang, H. , Matijevic, E. ' Interaction of Metal Hydrous Oxides with Chelating Agents. IV Dissolution of Haematite ' J. Colloid Interface Sci., 92, 479 (1983).

[5] Rubio, J. , Matijevic, E. ‘ Interaction of metal hydrous oxides with chelating agents. 1 β-FeOOH-EDTA ’ J. Colloid Interface Sci., 68, 408 (1979).

[6] Zhang, Y., Kallay, N. , Matijevic, E. ‘ Interaction of Metal Hydrous Oxides with Chelating Agents. 7 Haematite - Oxalic acid and - Citric acid Systems ’ Langmuir 1, 201 (1985).

[7] Blesa, M.A., Borohi, E.B., Regazzoni, A.E. , Maroto, A.J.G. ‘ Adsorption of EDTA & Iron-EDTA complexes on Magnetite and the Mechanism of Dissolution of Magnetite by EDTA ’ J. Colloid Interface Sci., 98, 295 (1984).

[8] Blesa, M. A., Marinovich, H. A., Baumgartner, E. C., ‘ Mechanism of Dissolution of Magnetite by Oxalic acid - Ferrous ion solutions ’ Inorg. Chem., 26, 3713 (1987)

[9] Torres, R., Blesa, M.A., Matijevic, E. ‘ Interaction of Metal Hydrous Oxides with Chelating Agents. VIII Dissolution of Haematite ’ J.Colloid Interface Sci., 131 , 567 (1989).

[10] Torres, R., Blesa, M.A., Matijevic, E. ‘ Interaction of Metal Hydrous Oxides with Chelating Agents. IX Reductive Dissolution of Haematite and Magnetite by Aminocarboxylic Acids ’ J. Colloid Interface Sci., 134, 475 (1990).

[11] Shailaja, M. , Narasimhan, S.V. ‘ Dissolution kinetics of Nickel Ferrite in Chelating and Reducing agents ’ J. Nucl. Sci.Technol., 28, 748 (1991).

[12] Shailaja, M. , Narasimhan, S.V. : ‘ Dissolution kinetics of Nickel Ferrite in Amino Poly Carboxylic Acids ’ J. Nucl. Sci.Technol., 28, 1107 (1991).

[13] Afonso, M.D.S., Morando, P.J., Blesa, M.A., Banwart, S., Stumm, W. ‘ The Reductive Dissolution of Iron Oxides by Ascorbate - The Role of Carboxylate Anions in Accelerating Reductive Dissolution ’ J. Colloid Interface Sci., 138, 74 (1990).

[14] Gilbert, R. , Quellet, L. ‘ Dissolution of Metal oxides accumalated in Nuclear Steam Generators : Study of Solutions containing organic chelating agents ’ Nuclear Tech., 68, 385 (1985).

[15] Segal, M.G., Sellers, R.M., ‘ Kinetics of Metal Oxide Dissolution Reductive Dissolution of Nickel Ferrite by Tris(picolinato) vanadium (II) ’ J. Chem. Soc. Faraday Trans., 1, 78, 1148 (1982)

[16] Kallay, N., Matijevic, E., ‘ Adsorption at Solid/Surfaces Interfaces 1. Interpretation of Surface Complexation of Oxalic and Citric acids with Haematite ’ Langmuir, 1, 195 (1985)

[17] O'Brien, A.B., Segal, M.G., Williams, W.J., ' Kinetics of Metal Oxide Dissolution Oxidative Dissolution of Chromium from Mixed Nickel-Iron-Chromium Oxides by Permanganate ' J. Chem. Soc. Faraday Trans. 1, 83, 371 (1987)

7 CREDITS

⇒ G. Venkateswaran, BARC
⇒ A. S. Gokhale, BARC
⇒ S. Joseph, BARC
⇒ H. N. Kansara, TAPS

XA9847489

DECONTAMINATION OF RADIOISOTOPE PRODUCTION FACILITY

M. DARYOKO, S. YATIM, H. SUSENO, M. WIRATMO
Radioactive Waste Management Technology Centre,
National Atomic Energy Agency,
Indonesia

Abstract

The strippable coating method use phosphoric glycerol and irradiated latex as supporting agents have been investigated. The investigation used some decontaminating agents : EDTA, citric acid, oxalic acid and potassium permanganate were combined with phosphoric glycerol supporting agent, then EDTA Na_2, sodium citric, sodium oxalic and potassium permanganate were combined with irradiated latex supporting agent. The study was needed to obtain the representative operating data, will be implemented to decontamination the Hot Cell for radioisotope production. The experiment used 50x50x1 mm stainless steel samples and contaminated by Cs-137 about 1.1×10^{-3} $\mu Ci/cm^2$. This samples according to inner cover of Hot Cell material, and Hot Cell activities. The decontamination factor results of the investigation were : phosphoric glycerol as supporting agent, about 20 (EDTA as decontaminating agent) to 47 (oxalic acid as decontaminating agent), and irradiated latex as supporting agent, about 11.5 (without decontamination agent) to 27 ($KMnO_4$ as decontaminating agent). All composition of the investigation have been obtained the good results, and can be implemented for decontamination of Hot Cell for radioisotope production. The irradiated latex could be recommended as supporting agent without decontaminating agent, because it is very easy to operate and very cheap cost.

INTRODUCTION

Triga Mark II Reactor on Bandung Nuclear Research Center was established and operated in 1965 with 250 KW power. Since 1971 the Research Reactor was upgraded to 1000 KW. The Nuclear Research Center was attached with a Hot Cell for a small scale production of radioisotopes and labelled compounds which was used from 1968. Some radionuclides were produced from raw materials and the formation reaction were shown in Table 1.

Since 1994, the Hot Cell facility was not used, because the production of radioisotope have been replaced by G.A. Siwabesy Multiple Reactor at Serpong site. However in the next a few years the Hot Cell might be used, because the increasing of demand of radioisotope and continue in their supply. For this purpose BATAN had been upgrading power the Triga Mark II Reactor from 1000 KW to 2000 KW. There are two alternatives for increasing radioisotope production, eventhough reuse of Hot Cell and to disposal of Hot Cell, for will change with new one. Both reusing and disposaling, decontamination work will necessary for decreasing radionuclides on the Hot Cell.

Table 1. Radioisotopes were produced in Hot cell

No	Radionuclide	Half time	Formation Reaction
1	P-32	14.28 d	${}_{16}S^{32}(n,p)\,{}_{15}P^{32}$
2	Cr-51	27.70 d	${}_{24}Cr^{50}\,(n,\gamma){}_{24}\,Cr^{51}$
3	Co-58	70.88 d	${}_{28}Ni^{58}\,(n,p)\,{}_{27}\,Co^{58}$
4	I-131	8.04 d	fission product of U-235 ${}_{52}Te^{130}\,(n,\beta)\,{}_{53}\,I^{131}$
5	Ir-192	74.40 d	${}_{77}\,Ir^{191}\,(n,\gamma)\,{}_{77}\,Ir^{192}$
6	Mo-99	67 h	fission product of U-235 ${}_{42}\,Mo^{98}\,(n,\gamma)\,{}_{42}\,Mo^{99}$
7	Na-24	15 h	${}_{11}\,Na^{23}\,(n,\gamma)\,{}_{11}\,Na^{24}$
8	Sc-46	84 d	${}_{21}\,Sc^{45}\,(n,\gamma)\,{}_{21}Sc^{46}$
9	Zn-65	245 d	${}_{30}\,Zn^{64}\,(n,\gamma)\,{}_{30}Zn^{65}$
10	Au-198	2.69 h	${}_{79}Au^{197}\,(n,\gamma)\,{}_{79}Au^{198}$
11	Br-82	1.471 d	${}_{35}\,Br^{81}\,(n,\gamma)\,{}_{35}\,Br^{82}$
12	Fe-59	45 h	${}_{26}\,Fe^{58}\,(n,\gamma)\,{}_{26}\,Fe^{59}$
13	Cu-64	12.8 h	${}_{29}\,Cu^{63}\,(n,\gamma)\,{}_{29}\,Cu^{64}$

BACKGROUND AND OBJECTIVES OF THE RESEARCH PROJECT

The relation with the decontamination planning, research and experience on the decontamination has been needed, both methodologies and techniques.

According to the Hot Cell using history could be predicted, that the Hot Cell wall activity is relatively low. This prediction will be surely if the characterisation work for the Hot Cell would be done. For this case, the water jetting methods that combine with detergent and chemical agent can be used. But this methods will be produced big volume of secondary waste.

The other methods, strippable coating methods hiphoteticaly is better. Some advantage will be carry out i.e: the application is very easy, suitable in situ decontamination, only use very little chemical (100 - 1000 g/m^2), a little volume of secondary waste (about 5 l/m^2), only solid waste produced, and avoid spread of contamination.

The strippable coating decontamination methods is developing from chemical decontamination methods, where the nuclides in the porous material were decontaminated by decontaminating agent in the supporting agent.

The strippable coating perform two functions : in addition to the incorporation of contaminants removed from the component surface, the film will fix activity, allowing decontamination to proceed section by section and preventing further contamination from adjacent work. In other word its mechanism are diffusion of decontaminating agent to the surface, decontamination and rediffusion of the decontaminating agent produced to the supporting agent.

Some materials have been used successfully as supporting agent such as poly ethylene, caseins, poly vinyl chlorida, phosphoric glycerol, phtalic glycerol. The coating can be used to prevent contamination of surface when applied prior to contamination, be used to remove surface contaminants when applied after contaminants is present. Several coats are usually necessary to provide sufficient strength to permit stripping from a surface.

In the research two kinds supporting agents would be used. First is phosphoric glycerol and second is irradiated latex. The phosphoric glycerol supporting agent usually have been used. It made from mixed between glycerin and phosphoric acid. The irradiated latex would be tried. It is natural latex have been irradiated by Co-60 Irradiator. Natural latex is poly isoprena polymer, and after have been irradiated will become crossed linking between poly isoprena one and the others. It have good characteristic : the adhesion effect to the metal is very small, very easy to implementation, and very easy to treatment of secondary waste.

Some decontaminants : EDTA, citric acid, oxalic acid, sodium EDTA, sodium citric, sodium oxalic and potassium permanganate would be used.

TECHNICAL APPROACH

The Hot Cell Characteristics.

The qualitative characterisation of Hot Cell have been carried out by non destructive analysis, both by smear test samples and in situ analysis by HpGe detector. The sampling points was shown in Table 2, including the place out the position of samples. The quantitative analysis was searched by smear test sample. The samples was counted by using GSM-10 and a HpGe detector coupled to MCA.

Decontamination

Decontamination experiment consisted of two kinds supporting agents. The supporting agent 1 is phosphoric glycerol. It made by mixing glycerin (87 % , s.g. 1.23) and phosphoric acid (89 %, s.g.1.75). The materials was heated about 1 hour and 100 ^{0}C. The materials will become to gel form. The supporting agent 2 is irradiated latex, produce by PAIR-BATAN. Decontaminating agents consisted of EDTA, citric acid, oxalic acid and $KMnO_4$ will be mixed with the supporting agents, either were varies : 0, 0.2, 0.5,1.0, 2.0 and 3.0 %.

The specimens were stainless steel 50x50x1 mm (the materials of specimen same with inner cover of Hot Cell wall) and was contaminated by Cs-137 about 1.1×10^{-3} $\mu Ci/cm^2$ (38 Bq). There is similar with Hot Cell activated. The decontamination factor was measured as a function of supporting agents kinds, decontaminating agent kinds and varies concentration of decontaminating agents. The start and final activity of specimen counted by detector NaI-Tl coupled by MCA.

The produces of the experiments will be implemented to decontaminated Hot Cell.

Table 2. The Hot Cell sample place

No Sample	Place	Position
1	Floor	Post North
2		Post East
3		Post South
4		Post West
5		Middle
6	Left Wall	Post North
7		Post East
8		Post South
9		Post West
10		Middle
11	Behind Wall	Post North
12		Post East
13		Post South
14		Post West
15		Middle
16	Right Wall	Post North
17		Post East
18		Post South
19		Post West
20		Middle
21	Front Wall	Post North
22		Post East
23		Post South
24		Post West
25		Middle
26	Upper Wall	Post North
27		Post East
28		Post South
29		Post West
30		Middle

ACCOMPLISHMENTS

The Hot Cell characteristic

The results of Hot Cell wall characterisation were shown on the table 3 and 4. It was shown that the activity of contamination levels of Hot Cell was ranging between 11.25 and 16.60 Bq/cm^2 ($3.04\text{x}10^{-10}$ - $4.40\text{x}10^{-10}$ Ci/cm^2). The activity has been based on the specimen activities.

In order to decontaminated down to unrestricted release (for the surface contaminated β/γ 3.7 Bq/cm^2) a decontamination factor larger than 10 must obtained reach a surface activity lower than 3.7 Bq/cm^2.

Table 3. Gross γ activity of Hot Cell by GSM-10

No	Activity, Bq/cm^2	No	Activity, Bq/cm^2
1	15.75	16	12.50
2	16.25	17	11.25
3	13.00	18	12.25
4	12.50	19	15.25
5	11.75	20	13.75
6	15.75	21	13.00
7	15.50	22	12.50
8	13.75	23	11.75
9	12.75	24	12.25
10	12.25	25	14.25
11	12.25	26	14.5
12	14.25	27	15.75
13	13.50	28	15.50
14	12.75	29	13.50
15	12.50	30	13.75

Table 4. The Radionuclides found in Hot cell Wall by MCA

No	Radionuclide	Half Time
1	K-40	$1.28\ 10^9$ y
2	Sc-46	84 d
3	Cu-64	12.8 h
4	Ga-67	78 h
5	Br-77	57 h
6	Y-87m	13 h
7	Ru-103	40 d
8	Er-171	7.8 h
9	Hf-171	12.2 h
10	Ir-192	13.83 d
11	Tl-208	3.1 m
12	Tl-208	1.32 m
13	Pb-212	10.6 h
14	Pb-214	26.8 m
15	Bi-124	29.7 m
16	Ra-226	1622 y
17	Th-227	18.6 d
18	Ac-228	6.13 h
19	Pa-234	1.175 m
20	U-235	$7.13\ 10^8$ y
21	I-131	8.04 d

Note : Total activity = 9 Bq/cm^2

Decontamination by phosphoric glycerol as supporting agent.

The phosphoric glycerol gel as supporting agent was prepared before. It was made from glycerin and phosphoric acid. Different composition of glycerin and phosphoric acid mixtures have been tested visually. It is in table 5. The result shown that the composition glycerin and phosphoric acid 10 : 5 is the best, and will be implemented for further experiments.

Table 5. Visually test from the gel formation

No	Glycerin : phosphoric acid	Visually test
1	10: 3	dissolved
2	10:4	paste form
3	10:5	paste form
4	10:6	gel form
5	10:7	gel form
6	10:8	gel form
7	10:9	gel form

In the table 6 shown that the decontamination factor that was measured as a function of operation time. The result shown that after processing for 30 minute, there were not significant changing of the decontamination factor. That happened, because the decontamination process that was begun from decontamination agent diffusion until re diffusion of decontamination product back the gel again trough water media or remain of glycerin and phosphoric acid solution. Therefore the process will finish after the gel was dried. After 30 minute, the increasing time does not effect of the decontamination factor .

Table 6. The influence of operating time
Decontaminating agent concentration 1 %

No	Decontaminating agent	Time (minutes)	A_o (Bq/cm^2)	At (Bq/cm^2)	DF
1	EDTA	30	52.17	2.87	18.18
2		45	40.48	2.38	17.22
3		60	52.86	3.06	18.18
4		75	62.10	3.33	18.65
5		90	53.37	2.79	19.13
1	citric acid	30	46.08	1.44	32.00
2		45	44.85	1.30	34.50
3		60	48.45	1.37	33.63
4		75	45.24	1.38	32.78
5		90	54.80	1.55	35.35
1	oxalic acid	30	52.64	1.23	42.80
2		45	48.27	1.13	42.72
3		60	50.40	1.18	42.72
4		75	45.36	1.06	42.80
5		90	50.38	1.18	42.70
1	$KMnO_4$	30	55.20	2.30	24.00
2		45	48.00	2.00	24.00
3		60	52.26	2.04	25.62
4		75	56.09	2.10	26.71
5		90	69.68	2.60	26.80

The influence of chemical agents concentration (0, 0.1, 0.5, 1.0, 2.0 and 3.0 %) could be shown on table 7. From the data shown, that the strippable coating process only by supporting agent, could influenced to decreasing of contaminant. It may be because between gel and contaminant has difference charge, therefore there are adhesion effect. Beside them, on the gel formation reaction still have remaining glycerin or phosphoric acid. Both glycerin and phosphoric acid could as chemical agent too.

Compared with citric acid , oxalic acid and potassium permanganate, EDTA is less aggressive decontaminating effect. It was caused by the decontaminating effect of EDTA only come from their complex agent form, whereas citric acid and oxalic acid have either acid solution, reduction solution and complex agent form.

Table 7 shown , that the decontamination factor was increased by addition of chemical agent concentrations. But after the concentration become 3 %, the increasing of decontamination factor doesn't mean anymore. It was happened because of the equilibrium between absorption, reaction on the film layer and desorption .

Table 7. The influence of decontaminating agent concentration
Supporting agent : phosphoric glycerol
Time : 1 hr

No	Decontaminating Agent	Concentration (%)	A_0 (Bq/cm^2)	At (Bq/cm^2)	DF
1	EDTA	0	52.25	5.93	8.80
2		0.1	54.15	3.31	16.38
3		0.5	53.20	2.92	18.18
4		1.0	52.80	3.06	17.27
5		2.0	54.15	2.98	18.18
6		3.0	58.90	2.95	20.00
1	citric acid	0	52.25	5.93	8.80
2		0.1	54.62	4.62	11.81
3		0.5	60.80	1.80	33.63
4		1.0	48.45	1.37	35.45
5		2.0	50.35	1.29	39.09
6		3.0	53.20	1.31	40.72
1	oxalic acid	0	52.25	5.93	8.80
2		0.1	40.27	1.70	23.63
3		0.5	42.40	1.23	34.54
4		1.0	50.40	1.18	42.72
5		2.0	52.80	1.16	45.45
6		3.0	53.20	1.13	47.27
1`	$KMnO_4$	0	52.25	5.93	8.80
2		0.1	48.10	2.13	22.55
3		0.5	54.26	2.39	22.71
4		1.0	52.16	2.04	25.62
5		2.0	47.28	1.69	27.97
6		3.0	49.10	1.77	27.80

Decontamination by irradiated latex as supporting agent

The using irradiated latex as supporting agent had much problems. The main problem is the difficulty of their mixing will chemical agent. The irradiated latex had small content ammonia for their establishment. Therefore some acid, oxalic acid, citric acid and EDTA would become ammonium salt, if the acid was added with irradiated latex. The ammonium salt form is coagulate. Table 8 shown the result mixing, between some chemical with irradiated latex.

Table 8. The mixing condition between irradiated latex and decontaminating agent

Decontaminating agent	After mixing condition
EDTA 1%	coagulate
EDTA-Na_2 1%	dissolve
citric acid 1%	coagulate
sodium citric 1%	dissolve
oxalic acid 1%	coagulate
sodium oxalic 1%	dissolve
$KMnO_4$	dissolve

This problems could be excelled by using chemical in the salt form, because the reaction between chemical agent and ammonia in irradiated latex was not hapenned.

Table 9 shown in influenced kinds and concentration of chemical agent, were irradiated latex as supporting agent. It is shown, that the decontamination factor was increased by addition of chemical agent concentration too.

The important opinion are decontamination only by irradiated latex, both as supporting and chemical agent. It could be shown on table 9 (concentration of decontaminating agent 0%). The other experiment were shown in table 10. Some activity samples were decontaminated by irradiated latex gel. The decontamination factor in the range of 8.61to 17.45.

Especially in this case, the decontamination factor of irradiated latex as strippable coating about 11.50, it had finished problem for using the Hot Cell decontamination.

Decontamination of Hot Cell

Although the execution of decontamination Hot Cell has not been done yet, but some points in the Hot Cell floor have tried to decontaminated by irradiated latex. The remaining activity of Hot Cell less than 1 Bq/cm^2. The fact shown, that the irradiated latex as strippable coating only, had finished problems for using the Hot Cell decontamination.

Table 9. The influence of decontaminating agent concentration
Supporting agent : irradiated latex
Operating time : 1 hr

No	Decontaminating agent	Concentration (%)	A_0 (Bq/cm^2)	At (Bq/cm^2)	DF
1	EDTA-Na_2	0	42.09	3.66	11.50
2		0.1	42.25	3.96	11.66
3		0.5	44.40	3.57	12.42
4		1.0	35.70	2.31	15.42
5		2.0	36.00	2.48	14.52
6		3.0	40.11	3.07	13.05
1	sodium citric	0	42.09	3.66	11.50
2		0.1	36.42	3.37	11.79
3		0.5	41.06	3.15	13.04
4		1.0	50.02	2.86	17.46
5		2.0	44.50	2.70	16.50
6		3.0	38.80	2.26	17.20
1	sodium oxalic	0	42.09	3.66	11.50
2		0.1	42.60	2.47	17.27
3		0.5	33.44	1.85	18.09
4		1.0	45.21	2.37	9.10
5		2.0	39.90	1.83	21.81
6		3.0	37.62	1.29	23.32
1	potassium permanganate	0	42.09	3.66	11.50
2		0.1	40.60	1.79	22.70
3		0.5	45.71	1.97	23.15
4		1.0	41.85	1.65	25.41
5		2.0	36.45	1.43	25.45
6		3,0	35.57	1.30	27.38

Table 10. Decontamination by irradiated latex
Sample : SS
Contaminant : Cs-137

No Sample	First Activity (Bq/cm^2)	Final Activity (Bq/cm^2)	FD
1	14.51	1.68	8.61
2	20.08	2.44	8.18
3	24.20	1.38	17.45
4	23.48	2.50	9.41
5	27.20	2.63	10.90
6	24.56	2.81	8.73

SUMMARY AND CONCLUSION

The highlighting investigation are :

- BATAN were upgrading power the Triga Mark II Reactor at Bandung Nuclear Research Center from 1000 kW to 2000 kW. There were to alternatives for increasing radioisotopes production , i.e : Reuse of Hot Cell or disposal of Hot Cell. To change the new one.

- The relation of that planing, research and experience on decontamination would be necessary, both methodologies and techniques.
- The characterisation of the Hot Cell have been done.
- The strippable coating methods, use general supporting agent (phosphoric glycerol) and specially supporting agent (irradiated latex) have been investigated. Some chemicals: EDTA, citric acid, oxalic acid, potassium permanganate and also their salt form were used as decontaminating agents.

The key results :

- The activity of the contamination levels of Hot Cell was ranging between 11 - 25 Bq/cm^2 (3.04.10^{-10} - 4. 40.10^{-10} Ci/cm^2).
- The decontamination factor results of the investigated as follows :
  - Phosphoric glycerol as supporting agent, about 20 (EDTA as decontamination agent) to 47 (oxalic acid as decontaminating agent).
  - Irradiated latex as supporting agent, about 11.5 (without decontamination agent) to 27 ($KMnO_4$ as decontaminating agent).
- All Composition of the investigated have been obtained the good results, and can be implemented for the Hot Cell decontamination.
- The irradiated latex could be recommended as both supporting agent and decontaminating agent. It is very easy to operate and very cheap cost.

REFERENCES

1. IAEA, "Decontamination of Water Cooled Reactors", Technical Report Series No. 365, IAEA, Vienna (1994)
2. LOMASNEY, LH., " Strippable Coating Help Reactor Cavity Decontamination", Nuclear Engineering International Magazine, September 1990, USA (1990).
3. SOFIARTI, W., "Produksi Lateks Karet Alam Radiasi", Buletin BATAN XIV (1), 27-31, Jakarta (1993).
4. IAEA, " Decontamination on Nuclear Facility to Permit Operation, Inspection , Maintenance, Modification or Plant Decommissioning", Technical Report Series no. 249 (1985).
5. IAEA, " Status of Technology for Volume Reduction and Treatment of Low and Intermediate Level (1994).
6. DARYOKO, M., " Dekontaminasi Strippable Coating Baja Tahan Karat Menggunakan Bahan Penopang Gel Gliserofosfat", Prosiding Hasil Penelitian PTPLR, ISSN 0852 2979, 113-118, Jakarta (1997)
7. SUSENO, H., " Penggunaan Lateks Iradiasi Sebagai Bahan Penopang Pada Dekontaminasi dengan Tehnik Strippable Coating", Prosiding Hasil Penelitian PTPLR, ISSN 0852 2979, 119-123, Jakarta (1997).
8. LURIE, R., "Decontamination of The Main Circuits of The G2 Gas Graphite Reactor" IAEA-TecDoc-511, 47-53, Vienna, 1989

XA9847490

EFFECTIVENESS OF DIFFERENT DECONTAMINATION TECHNIQUES ON METALLIC SCRAPS ARISING FROM DECOMMISSIONED POWER PLANTS

E. BORIOLI, F. BREGANI, A. GAROFALO
Nuclear Energy Division,
Italian Electricity Company, Milan,
Italy

Abstarct

The report summarizes the results obtained from the metallographic characterization and decontamination tests performed on metallic scraps coming from Latina, Caorso and Trino Vercellese nuclear power plants.

To evaluate the amount of the contamination that could be lost during the manipulation of a sample (i.e. packaging, transport, cutting ecc.), supplemental radiometric measurements were performed on the sample provided by Trino V. before and after its cutting in the laboratory. The results show that either joint ultrasonic and chemical decontamination or electrodecontamination are very effective techniques in removing contamination, and the amount of the contamination lost during the manipulation of the Trino V. sample, if occurred, is not greater than 5-10%.

1. INTRODUCTION

The activity was intended to characterize the contamination layers on metallic scraps coming from Latina, Caorso and Trino Vercellese nuclear power plants, either in morphology or in mechanical properties, in order to address proper conservation methods and as a precursor for future decontamination activities.

Latina is a gas cooled reactor power plant equipped with a single 705 MWt (200 MWe) Magnox reactor, located in the central part of Italy on the Tyrrhenian sea. The coolant is CO2 in closed circuit; it goes through the core from the bottom to the top.

Caorso is a nuclear power plant located in the northern part of Italy, equipped with a boiling water reactor of 2650 MWt (860 MWe); Trino Vercellese is a nuclear power plant located in the northern part of Italy, equipped with a pressurized water reactor of 870 MWt (270 MWe).

After the November 1987 referendum, the Italian Government decided to stop all the plants and the owner was ordered to start the procedures to bring them into a passive protective condition.

All the samples provided by the plants have been cut into small pieces (specimens): some of them have been used in the decontamination tests and some in the metallographic characterization. The results of the decontamination tests are related to the Co-60.

All the activities were conducted in the JRC laboratories at Ispra.

As there is the possibility that part of the contamination could be lost during the manipulation of the samples, i.e. packaging, transport, cutting etc., supplemental radiometric measurements were performed on the sample provided by Trino V. before and after its cutting, in order to evaluate the amount of the contamination that could be lost during these operations.

2. EXPERIMENTAL

2.1 Decontamination tests

The decontamination tests performed can be grouped in two categories:

1 - *Tests to evaluate the consistence and the adherence of the oxide by using mechanical actions (air flow, wiping, ultrasonic cleaning);*

2 - *Tests to evaluate the effectiveness of chemical processes alone or combined with mechanical or electrical actions (soft chemical decontamination, aggressive chemical decontamination, joint ultrasonic and chemical decontamination, electrodecontamination).*

Acid solutions and operating conditions have been established according to the results of analogous experience in the past.

Air flow: this test enables to evaluate the volatile fraction of the deposit that could be accidentally resuspended during dismantling, transport and packaging operations.
The apparatus consists in a pump-generated air flow that impinges on the specimen at 17, 23, 35 and 46 m/s, at room temperature for 30 minutes.

Abrasive wiping: this test enables to evaluate the smeareable fraction of the deposit.
Wiping was performed with a sheet of paper, 3 m long with an average speed of 0.25 m/s and 100 g/cm^2 load.

Ultrasonic cleaning: this test removes the more adherent deposit. The specimen is housed in a beaker filled with water, placed in a ultrasonic tank containing water.
Operating parameters were: 40 KHz frequency, 25 W/l specific power, 60 minutes test time at room temperature.

Soft chemical decontamination: this test was carried out using a mixture of oxalic and citric acid 3+3% at 80 C for 360 minutes.

Aggressive chemical decontamination: this test dissolves part of the deposit, the oxide and the base material.
It was performed using a mixture of 3% hydrofluoric and 15% formic acid at room temperature for 120 minutes.

Joint ultrasonic and chemical decontamination: the test was performed using a mixture of 3% hydrofluoric and 15% formic acid in the ultrasonic tank previously described, at room temperature for 90 minutes.

Electrodecontamination: the test was performed using a mixture of 3% hydrofluoric and 15% formic acid in a beaker with a current density of 60 mA/cm^2, at room temperature for 60 minutes.

2.2 Metallographic characterization

Metallographic characterization has been carried out using scanning electron microscopy (SEM), optical microscopy (OM) and electron micro-probe analysis with an X-ray spectrometer working on the energy dispersion principle (EDS).
The specimens used in the cross section optical microscopy and SEM analysis were embedded in a slowly hardening epoxy resin. After 24 hours hardening, they were polished with papers and diamond pastes.

Next sections illustrate the results obtained for each plant.

3. EXPERIMENTAL RESULTS FROM LATINA

3.1 Nature of the samples

The samples provided by the plant are in carbon steel and consist of 4 pieces of finned tubes, 70 mm diameter and 120 mm long, and 2 pieces of plate, 150 x 110 x 5-8 mm, taken from boiler n.2.

Table 3.1.1 - Characteristics of the samples from Latina

Sample N.	2	4	5	6	7	8
Shape	F. T.	Plate	F.T.	F.T.	F.T.	Plate
Weight (g)	1450	950	1200	1200	1450	800
Oper. temp (C)	360	360	190	220	325	255
Int. press. (bar)	13.8	-	6.5	13.8	46	-
Ext. press. (bar)	12.5	12.5	12.5	12.5	12.5	12.5
Co-60 (Bq/cm^2)	23	23	4.5	5.3	21	21
Cs-137(Bq/cm^2)	8.5	8.5	2.5	4.1	18	18
Sr-90 (Bq/cm^2)	8.3	8.3	1.1	1.8	23	23
Fe-55 (Bq/cm^2)	120	120	21	30	70	70

F.T. = Finned tube

All the samples were cut into small specimens. Part of them were used for metallographic characterization and part for decontamination tests.

3.2 Metallographic characterization results

Sample N.2

The surface is covered with a uniform black deposit. The particle size is 1 μm for single particles and 5-10 μm for agglomerates. The average composition of the deposit is 44% Fe; 23% O_2; 29% C, measured on the surface, and 44% Fe; 40% O_2; 15% C, measured on the cross section .

The thickness of the oxide is 40-50 μm on the fin surface and 200 μm at the base of the fins.

Sample N.4

Both sides of the surface are covered with a black deposit. The particle size is 1 μm for small particles, 3-5 μm for agglomerates and 20 μm for large particles.

The average composition measured on the surface of the deposit is 31% Fe; 18% O_2; 45% C.

The thickness of the oxide is 100-150 μm, with high carbon concentration particles embedded.

Sample N.5

The surface is covered with a non uniform, friable and scarcely adherent deposit.

To obtain more significant information, the characterizations were performed on three specimens:

Specimen N.83: is covered with a uniform black deposit. The particle size is 1-3 μm for single particles; 10-15 μm for agglomerates and large particles. No significant oxide thickness;

Specimen N.93: is covered with a very thin deposit and spongy islands. The particle size is 5 μm. No significant oxide thickness;

Specimen N.95: is covered with a very thin deposit. The particle size is 5 μm. The thickness of the oxide is 30-50 μm.

Sample N.6

The surface is covered with a black deposit. The particle size is 1-2 μm for single particles and 5-10 μm for agglomerates.

The average particle composition is 20% Fe; 23% O_2; 55% C.

The thickness of the oxide is 40-50 μm on the fin surface and 250 μm at the base of the fins.

Sample N.7

The surface is covered with a black deposit with white particles. The particle size is 1-3 μm for single particles and 5-10 μm for large particles and agglomerates.

The average particle composition is 60% Fe; 20% O_2; 20% C.

Thickness of the oxide on the fin surface is 30-50 μm.

Sample N.8

Both sides of the surface present a uniform black deposit, consisting of large islands of 100-200 μm partially covered with 1-3 μm for particles.

The thickness of the oxide is 100-150 μm on both surfaces.

3.3 Decontamination test results

The following table reports the results of the average, the maximum and the minimum value of the decontamination efficiency referred to all the samples:

Table 3.3.1 - DE% for the samples from Latina

Decontamination test	DE% (ave)	DE% (max)	DE% (min)
Air flow	12.6	26.5	3.6
Abrasive wiping	59.8	99.3	33.1
Ultrasonic cleaning	62.1	94.6	6.7
Soft chemical decontamiantion	13.2	25.0	3.0
Aggressive chemical decont.	45.7	85.8	12.9
Joint ultrasonic & chemical decont.	84.9	99.4	51.4
Electrodecontamination	58.6	96.6	22.7

DE% = (1-Af/Ai)*100 Ai = count rate before the test; Af = count rate after the test

3.4 Conclusions on Latina samples

An average of 60% of Co-60 contamination can be removed by weak mechanical actions. Aggressive chemicals provided an average DE% around 50%. The best results were obtained by means of the joint ultrasonic and chemical technique, that provided an average DE% around 85%.

The oxide thickness is:

- 100-150 μm on the plate samples;
- 30-50 μm on the fin surface of the tubes;

- 200-250 μm on the base of the tubes.

The deposit and the oxide contain some particles probably coming from the graphite in the moderator.

4. EXPERIMENTAL RESULTS FROM CAORSO

4.1 Nature of the samples

Part of the samples provided by the plant are in stainless steel and part in carbon steel. They consist of seal disks of stop valves coming from an auxiliary line of the main steam system (N22), from clean up (G33), spent fuel pool (G41), radwaste (G11) and feedwater (N21) systems.

Table 4.1.1 - Characteristics of the samples from Caorso

Sample N.	1	2	3	4	5
System	G33	N22	G41	G11	N21
Material	SS	CS	SS	CS	CS
Oper. temp (C)	35-130	150-160	25-40	25-30	30-40
Press. (bar)	20-90	4	6	4	6-7
Co-60 (Bq/cm^2)	3.0E4	0.5	1.2E3	3.5E3	1.5

SS = stainless steel; CS = carbon steel

All the samples were cut into small specimens and the two horizontal sides were named “A” and “B”, where the side “A” corresponds to the opposite of the seal face of the shutter disk and the side “B” corresponds to the seal face of the shutter disk. Part of the specimens were used for metallographic characterization and part for the decontamination tests.

4.2 Metallographic characterization results

Sample N.1 (stainless steel)

The surface is covered with a uniform deposit and the average particle size is 10 μm. The EDS analysis indicates the presence of clorides and sulphates of Al, Na, K, probably originated by the evaporation of water on the surface of the sample.
The oxide is too thin to be measurable.

Sample N.2 (carbon steel)

The surface is covered with a deposit and the average particle size is 1.5 μm.
Measurements of the oxide thickness performed on two specimens gave the following results:

specimen N.1: two layers of 20 and 125 μm on side A and one layer of 10 μm on side B;

specimen N.2: three layers of 15, 50 and 150 μm on side A and one layer of 1.5 μm on side B.

The difference in the thickness of the oxide on the two sides of the same specimen is due to their different operation conditions.

Sample N.3 (stainless steel)

The surface is covered with a non uniform deposit. Two kinds of particles are found on the deposit: small particles of 0.5 μm containing Fe, Ni, Cr and Si and bigger particles of 5 μm containing a mixture of iron oxides and in some cases also Si and Mg.

The thickness of the oxide is 25 μm on side A and 3 μm on side B.

Sample N.4 (carbon steel)

The surface is covered with a deposit of mixed iron oxides; the average particle size is 3.5 μm. The analysis indicates the presence of silicon.

The thickness of the oxide, measured in this sample only on side B is 10 μm.

Sample N.5 (carbon steel)

The surface is covered with a uniform deposit. The average particle size is 2 μm.

The cross section analysis shows that there are two layers of oxide, 45 and 100 μm thick on side A and one layer of 15 μm on side B.

4.3 Decontamination test results

The tests have been performed separately on side A and B of each specimen and the results are summarized in the following table:

Table 4.3.1 - DE% for the samples from Caorso

Decontamination test	Side A			Side B		
	DE% (ave)	DE% (max)	DE% (min)	DE% (ave)	DE% (max)	DE% (min)
Air flow	34.1	63.6	5.4	25.0	63.6	3.3
Abrasive wiping	82.9	95.8	72.7	81.0	87.1	72.7
Ultrasonic cleaning	61.8	97.5	11.7	82.2	88.0	76.9
Soft chemical decont.	58.0	79.0	41.1	49.2	40.4	55.5
Aggressive chemical decont.	91.4	99.9	80.6	72.7	99.2	22.1
Joint ultrasonic & chemical dec.	97.7	99.9	90.9	97.1	99.9	90.9
Electrodecontamination:	95.1	99.7	90.9	94.2	99.9	90.9

DE% = (1-Af/Ai)*100   Ai = count rate before the test; Af = count rate after the test

4.4 Conclusions on Caorso samples

More than 80% of the Co-60 contamination can be removed by weak mechanical actions. Joint ultrasonic & chemical technique and electrodecontamination are very effective and remove more than 94% of the contamination.

Part of the oxide on the samples comes from other systems of the plant.

The oxide thickness on the two sides is different (about one order of magnitude), because of their different operation conditions. Further, the oxide on side B has a lower thickness than that on side A and samples in carbon steel have an oxide thickness greater than that of samples in stainless steel.

The contamination is not uniformly distributed on the surface of the samples.

There is no evidence of localized corrosion on the samples.

5. EXPERIMENTAL RESULTS FROM TRINO VERCELLESE

5.1 Nature of the sample and contamination loss evaluation

The sample provided from the plant is a part of an electrical heater of the pressurizer and consists of a stainless steel tube, 400 mm long, ϕ = 17 mm.

Table 5.1.1 - Characteristics of the sample from Trino V.

Material	SS
Oper. temp (C)	336
Press. (bar)	140.6
Co-60 (Bq/cm^2)	1.7E4

Other than metallographic characterization and decontamination tests, on this sample it has been measured also the amount of contamination that could have been lost during its manipulation in the laboratory.

The procedure used for the measurement followed these steps:

a) evaluation of the counting profile along the axis of the sample: this was performed using a NaI detector with a lead shield 2 m long and 4 cm thick between the detector and the sample. The shield has a hole of 2.5 cm in diameter to allow to count the Co-60 radiation from the portion of the sample in front of the detector, as illustrate in Fig.5.1.1

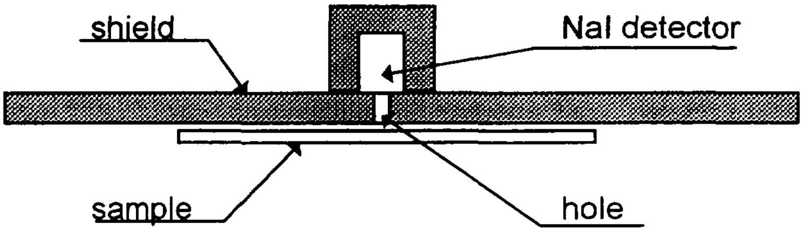


Fig. 5.1.1 - Measurement system

b) evaluation of the contamination profile along the axis of the sample: this was obtained subtracting to the counts of the portion of the sample in front of the detector the counts due to the radiation coming from the other portions of the sample that crosses the shield and reaches the detector.

For this purpose, it has been necessary to determine experimentally a "transfer function", which value for a generic position is defined as the ratio between the counts of a source placed in that position and the counts of the same source when placed in front of the detector, as shown in Fig.5.1.2.

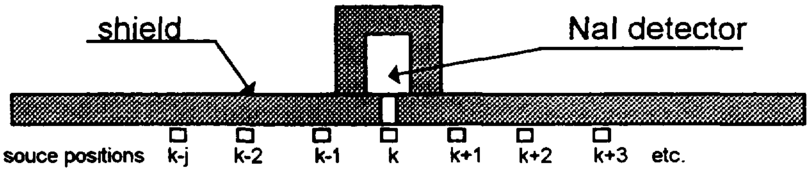


Fig. 5.1.2 - Positions of the source to determine the transfer function

As an example, in position k-1 it is: $f(k-1) = counts(k-1)/counts(k)$.
By definition, $f(k) = 1$.

The counts for each portion of the sample when faced to the detector is given by:

$$Cm(k) = f(k) \cdot C(k) + f(k+1) \cdot C(k+1) + f(k+2) \cdot C(k+2) + \ldots f(k+j) \cdot C(k+j) + \ldots\ldots$$
$$+ f(k-1) \cdot C(k-1) + f(k-2) \cdot C(k-2) + \ldots f(k-j) \cdot C(k-j) + \ldots\ldots$$

where:

$Cm(k)$	are the counts measured for the portion K in front of the detector. They include the contribution of the other portions of the sample not faced to the detector;
$C(k \pm j)$	are the counts (unknown) for the portion $K \pm j$ when placed in front of the detector, without the contribution of the other portions;
$f(k \pm j)$	are the values of the transfer function in each position.

Applying these equation to each portion of the sample, one obtains a linear system of equations that can be easily solved and the solution gives the counts for each portion due to its contamination, without the contribution of the other portions.

c) cutting of the sample into 16 specimens (numbered for other practical reasons from 5 to 20), each 2.5 cm long;

d) counting of each specimen and comparison with the counts of the sample portion corresponding to the position occupied by the specimen before cutting the sample, obtained from the system of equations described before.

The difference between b) and d) is related the amount of the activity lost during the manipulation of the sample.

The following table shows the ratios between the counts before and after the cut of the sample:

Table 5.1.2 - Ratios of the counts before and after the cut

Specimen number	$\frac{\text{bef. cutting}}{\text{aft. cutting}}$	Specimen number	$\frac{\text{bef. cutting}}{\text{aft. cutting}}$
5	1.379	13	0.971
6	1.617	14	0.897
7	1.197	15	0.996
8	1.108	16	0.891
9	0.965	17	0.936
10	0.961	18	0.930
11	1.132	19	1.005
12	0.828	20	0.828

In there would be no loss of contamination, all the ratios should be 1. Instead, the results are sometimes greater than 1 and sometimes lower than 1.
When the ratio is greater than 1 this is due to the sistematic and statistical errors connected to the measurements, while when the ratio is lower than 1 it is not possible to say if this is due to the errors or to a loss of contamination.
In any case it is possible to say that if there was a loss of contamination this is not greater than 5-10%.

5.2 Metallographic characterization results

Specimen N.6

The surface is covered with a non uniform deposit consisting in mixed chromium and iron oxides. The average particle size is 2-4 μm. Supplemental XRD analysis indicates that the iron oxide in mainly in the magnetite form.

The cross section analysis shows two layers of oxide: the inner one is 2 μm thick with presence of chromium oxides, the outer one is 7 μm thick.

Specimen N.15

The surface is covered with a deposit. The particle size is in the range 0.1-5 μm.

The cross section analysis shows only one layer of oxide 2 μm thick.

XRD analysis indicates that the iron oxide is magnetite.

5.3 - Decontamination test results

The results obtained in the decontamination tests are reported in the following table:

Table 5.3.1 - DE% for the sample from Trino V.

Decontamination test	DE% (ave)	DE% (max)	DE% (min)
Air flow	3.8	5.5	2.1
Abrasive wiping	30.7	40.7	20.7
Ultrasonic cleaning	25.6	30.7	20.4
Soft chemical decont.	12.6	16.3	8.9
Aggressive chemical decont.	60.8	67.8	53.8
Joint ultrasonic & chemical dec.	84.9	88.2	81.6
Electrodecontamination:	99.9	99.9	99.9

DE% = (1-Af/Ai)•100   Ai = count rate before the test; Af = count rate after the test

5.4 Conclusions on Trino V. sample

More than 30% of Co-60 contamination can be removed by weak mechanical actions. Aggressive chemicals remove about 60% of the contamination, joint ultrasonic and chemical technique about 85%.

Electrodecontamination is very effective and removes more than 99% of the contamination.

XRD analysis indicates that part of the oxide is magnetite.

The loss of contamination during the manipulation of the sample in the laboratory, if it occured, is not greater than 5-10%.

6. SUMMARY

The activity was performed to characterize stainless steel and carbon steel samples provided by a GCR, a BWR and a PWR nuclear power plants. Each sample has been characterized either in morphology or in mechanical properties.

Joint ultrasonic & chemical technique and electrodecontamination appear to be a very effective tools and remove the most of the contamination.

On the sample provided by Trino V. it has been also evaluated the amount of contamination lost during the manipulation in the laboratory. The results show that it is not greater than 5-10%.

REFERENCES

1. I. Ciaccolini: "Determinazione di Fe-55, Ni-59, Ni-63, Sr-90", Rapporto Topico CISE n.5954, 24 Gennaio 1991
2. F.Bregani, G.P.Toledo: "Caratterizzazione di Materiali Contaminati Provenienti dal Generatore di Vapore n.2 della Centrale Elettronucleare di Latina", Rapporto ENEL/CRAM T11/94/02, Giugno 1994
3. E.Borioli, F.Bregani, G.Sandrelli "Caratterizzazione di Materiali Contaminati Provenienti dalla Centrale Elettronucleare di Caorso - Rapporto Finale", Rapporto ENEL/ATN/GNUM, 31 Maggio 1995
4. P.A.Borroni: "Caratterizzazione di Materiali Contaminati Provenienti dalla Centrale Elettronucleare di Trino Vercellese", Rapporto CISE-SCC-95-68, 9 Gennaio 1996
5. M. Della Rossa, G. Marcon: "Caratterizzazione di Materiali Contaminati e Messa a Disposizione di un'Area Sperimentale Attrezzata per Prove di Decontaminazione e Misure ai Fini del Decommissioning. Parte II", Rapporto N.E. 11.6302.A.013 Rev.0, 29 Febbraio 1996 (Rapporto finale relativo al Contratto di Ricerca tra ENEL S.p.A/DSR/VDN e CCR-Ispra n. 2GNSI0003 per ENEL e n. 10422-94-08 T1ED ISP I per CCR-Ispra)
6. E.Borioli, G.Sandrelli: "Caratterizzazione di Materiali Contaminati Provenienti dalla Centrale Elettronucleare di Trino Vercellese (Riscaldatore elettrico del Pressurizzatore)", Rapporto ENEL, 30 Maggio 1996

XA9847491

TECHNOLOGY FOR REUSE OF CONTAMINATED CONCRETE CONSTITUENTS

I.P. BINKHORST, H.A.W. CORNELISSEN
Environmental Technology Department, KEMA,
Netherlands

Abstract

During decommissioning activities of nuclear installations, large amounts of contaminated concrete will have to be processed. All this concrete has to be treated and stored as radioactive waste, which implies major economical and environmental consequences.

It was shown that the contamination is mainly concentrated in the porous cementstone. By separating this cementstone from the clean dense aggregate particles, a considerable volume reduction can be reached. KEMA has developed, designed and constructed a pilot plant scale test installation for separation of aggregate from contaminated concrete. The separation is based on a thermal treatment followed by milling and sieving.

The clean aggregate can be re-used in concrete, whereas the (slightly) contaminated cementstone could be upgraded to a binder for concrete used in the nuclear industry.

INTRODUCTION

In a nuclear installation, concrete in various building structures may get contaminated during operation. When the installation is withdrawn from service and eventually dismantled the contaminated concrete has to be conditioned and disposed off as radioactive waste. In many countries the disposal of waste coming from nuclear power plants is a major point of concern. Therefore, research is necessary to look into the possibilities for volume reduction and the re-use of material as an alternative solution for "waste" storage.

It was found that volume reduction of contaminated concrete can be achieved by separation of the fine cement stone and coarse gravel (Cornelissen, 1995). Subsequently the possible re-use of the cement stone (being fine material) was investigated. The fine material (waste) was upgraded for re-use as a cementitious binder or as a filler in building materials.

In the framework of the European Communities Programme on Decommissioning, KEMA (Netherlands) cooperated with CEA-UDIN (France) and BNFL (UK) in the project called RE-BONDIN.

BACKGROUND AND OBJECTIVES OF THE RESEARCH PROJECT

KEMA has developed, designed and constructed a pilot plant scale test installation for volume reduction of contaminated concrete. The solidification of the residual waste was studied by Taywood Engineering. From Versuchs Atomkraftwerk Kahl support was given to test the installation under actual conditions. The project was performed in the period 1989 - 1994 (Cornelissen, 1995).

In a nuclear installation, concrete in various building structures may get contaminated during operation When the installation is withdrawn from service and eventually dismantled the contaminated concrete has to be conditioned and disposed off as radioactive waste Global calculations indicate that per reactor about 3000 to 4000 tons will have to be conditioned

In many cases, mainly the surface layer of the concrete structure will be contaminated So a huge volume reduction can be obtained by removing this layer The remaining structure can be treated as a clean building Depending on environmental and economical conditions the concrete of the surface layer can be processed in a second step in order to gain maximum volume reduction of contaminated concrete (see figure I)

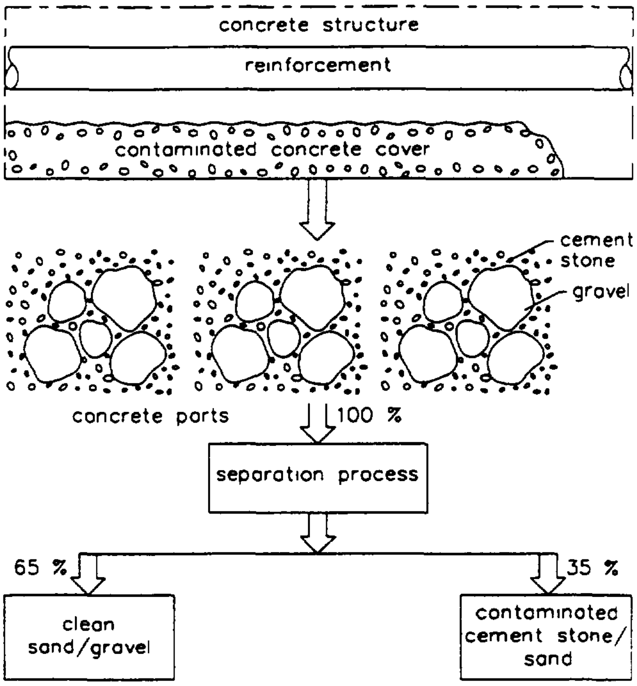


Figure I Removing the contaminated concrete layer followed by separation

After processing, the gravel can be re-used. In the on-going project, in which KEMA cooperates with CEA and BNFL, the possibilities for re-use of cementstone are being tested. The use of this material as binder for concrete in the nuclear industry seems promising.

The ultimate objective of the project is to reduce the volume of contaminated concrete, by separation techniques and re-use for the residues.

TECHNICAL APPROACH

Concrete contamination and activation

In normal quality concretes, the volume of the porous cementstone is approximately 30%, while the remaining part consists of dense aggregates such as quartz and limestone Tests have shown that contamination primarily penetrates in the cementstone (see figure II) Separation of the porous and dense components of concrete will therefore result in substantial volume reduction of radioactive waste. This is beneficial for economical and environmental reasons.

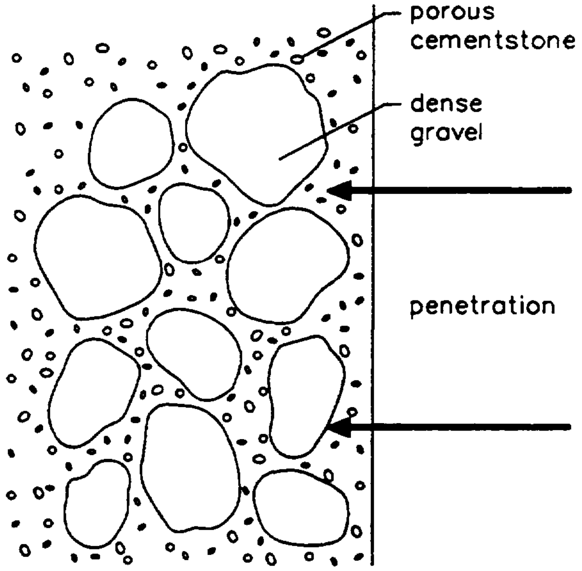


Figure II Contamination of the porous component of concrete

In order to verify the assumption that mainly porous cementstone is contaminated, concrete samples were supplied by the Borssele and Dodewaard nuclear power plants in the Netherlands. The Borssele sample was taken from a concrete element which was used in a room were the handling with radioactive fluids took place.

The main nuclide was ^{60}Co, which caused a total radioactivity of 120 kBq (0,23 kBq/g). The Dodewaard sample, from a core, was especially contaminated for these tests. therefore the core was submerged in radioactive water (150 kBq/l) consisting mainly of ^{137}Cs, ^{60}Co and ^{54}Mn. The total amount of radioactivity of the sample measured with a Germanium detector was 137 Bq for ^{60}Co (0,34 Bq/g), 700 Bq for ^{137}Cs (1,76 Bq/g) and 827 Bq for ^{54}Mn (2,1 Bq/g).

Both concrete samples were separated according to the following procedure:

a grinding and separation by sieving
b washing in HNO_3
c grinding again and separation by sieving
d washing in HCl
e selection (visual) of aggregates just covered with a low or no percentage of cementstone remainings.

After each separation step the activity of the components was measured. The results with respect to ^{60}Co are given in table I.

With respect to ^{60}Co, it can be derived from table 1, that the remaining activity of the aggregates after process step d is about 10 times smaller than the activity of the concrete samples, being 120 kBq and 137 Bq for the Borssele and Dodewaard sample respectively.

Table I Separation of contaminated and non-contaminated parts (activity due to ^{60}Co)

Borssele sample	aggregates (kBq)		cementstone (kBq)		residue* (kBq)
separation step					
a	59	(0,15)**	65	(0,50)	-
b	19	(0,05)	-		34
c	14	(0,04)	-		5
d	12	(0,04)	-		3
e	4	(0,03)	-		-
Dodewaard sample	**aggregates (Bq)**		**cementstone (Bq)**		**residue* (Bq)**
separation step					
a	59	(0,20)	84	(0,85)	-
b	13	(0,06)	-		49

* cementstone, leaching fluid, filter residue

** specific activity (kBq/g and Bq/g)

For the other nuclides, reduction factors were found being 5 for ^{137}Cs and 16 for ^{54}Mn. in terms of specific activity the reduction factors turned out to be 6 for ^{60}Co, 3 for ^{137}Cs and 9,5 for ^{54}Mn.

From the verification tests it can be concluded that the contamination of concrete is mainly concentrated in the porous cement stone.

In these tests the separation process was not yet optimized, therefore further improvement of the separation can be expected by the application of an appropriate technique as described in the following chapters.

Also the possible activation of concrete was tested. Therefore the various concrete components were subjected to a neutron fluency of $2{,}5 \times 10^{23}$ n/m^2. Ordinary Portland Cement (OPC) and Portland Blastfurnace Cement (PBC) were used. The tested aggregates were quartz, limestone and barite. The results as presented in table II show that because of their chemical composition, quartz gravel and limestone are less susceptible to activation than cements, while barite shows the opposite. From the tests it can be concluded that separation of contaminated concrete is effective. This is also true for activated quartz and limestone concretes.

Basics of separation

Separation of concrete into its components gravel, sand and cementstone is based on the reduction of bond between the cement matrix and the aggregates. The bond can be reduced by temperature induced mechanical stresses. Two methods were tested in this research programme. Cooling down by liquid nitrogen and heating up in an oven. The latter method has an additional chemical effect because of decomposition of the cementstone.

Table II Results of irradiation tests (2,5 x 10^{23} n/m^2)

component	activity after 2y decay (MBq/kg)
cement:	
Ordinary Portland	88
Portland blast furnace	84
aggregate:	
quartz	5
limestone	27
barite	122

Typical results of both temperature treatments are presented in table III in terms of the separation efficiency, E_d, defined as:

$$E_d = A_s / A_o$$

In this formula A_s stand for the separated material smaller than 1 mm, while A_o represents the original amount of cementstone and sand smaller than 1 mm (the separated "waste"). It can be seen that heating up is more effective.

Table III Effect of type of temperature treatment on separation

thermal treatment	E_d (%)
heating up (650 °)	80
cooling down (liquid N_2)	39

In the research programme, important concrete and process variables on concrete separation were investigated. This finally led to a setup for a separation plant as schematically presented in figure III. In this figure, four main steps can be distinguished. In the first step concrete parts are crushed in order to extend the surface assessable for the subsequent treatments. By means of heating up, the bond between aggregate and cement matrix is reduced and in the next step separation is realized by mechanical forces in a turning mill. Then a selection has to be made between contaminated and clean material. It was decided from preceding tests, to sieve the material over 1 mm sieves. The material < 1 mm turned out to contain the powdered cementstone and consequently the contamination.

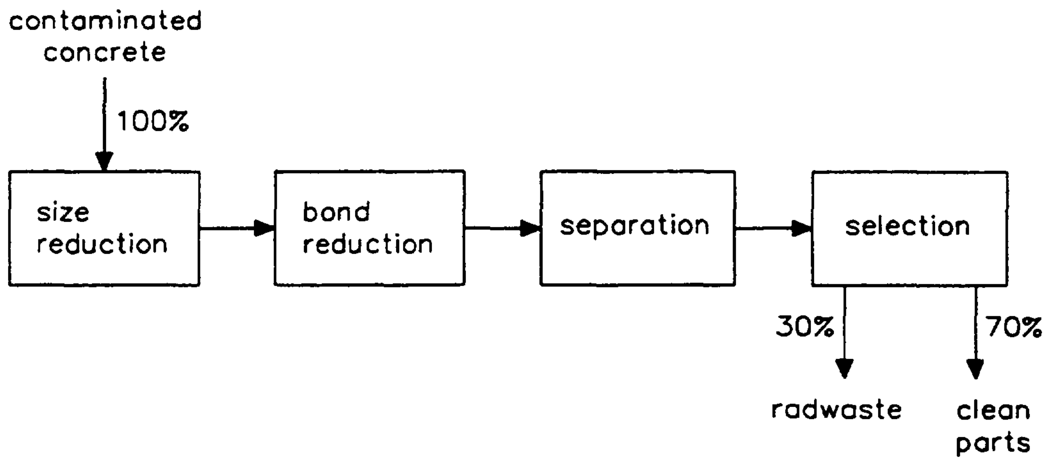


Figure III Flow sheet of concrete separation process

Pilot plant scale test installation

The approach as presented before in figure III formed the basis for the design of a pilot plant scale test installation for separation of contaminated concrete.

In order to be able to use standard components, a batch-wise process was developed. Much attention was given to dust-free operation, which resulted in the introduction of closed process containers and a filtering system connected to all individual components. In the process flow diagram of figure IV, the various components and the process are shown. An additional important feature of this installation is that all process parameters can be investigated in a wide range.

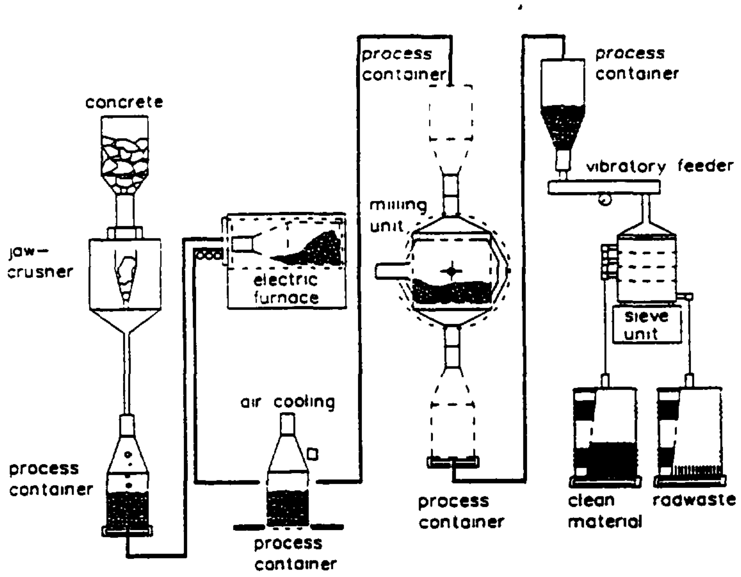


Figure IV Process flow diagram of the test installation

In the jaw-crusher the input concrete is crushed to about 40 mm diameter parts, which are then transported in a specially designed closed process container to the electrical oven for a temperature treatment at about 650 °C. After cooling down of the concrete, the mill (in vertical position) is loaded and then operated (in horizontal position). In the last step the milled material is led to the sieve unit, where the cementstone and fine sand < 1 mm is collected as radwaste in a storage drum. The material > 1 mm is also collected for possible reuse as concrete aggregate. A top view of the installation as erected in the KEMA laboratories is shown in figure V.

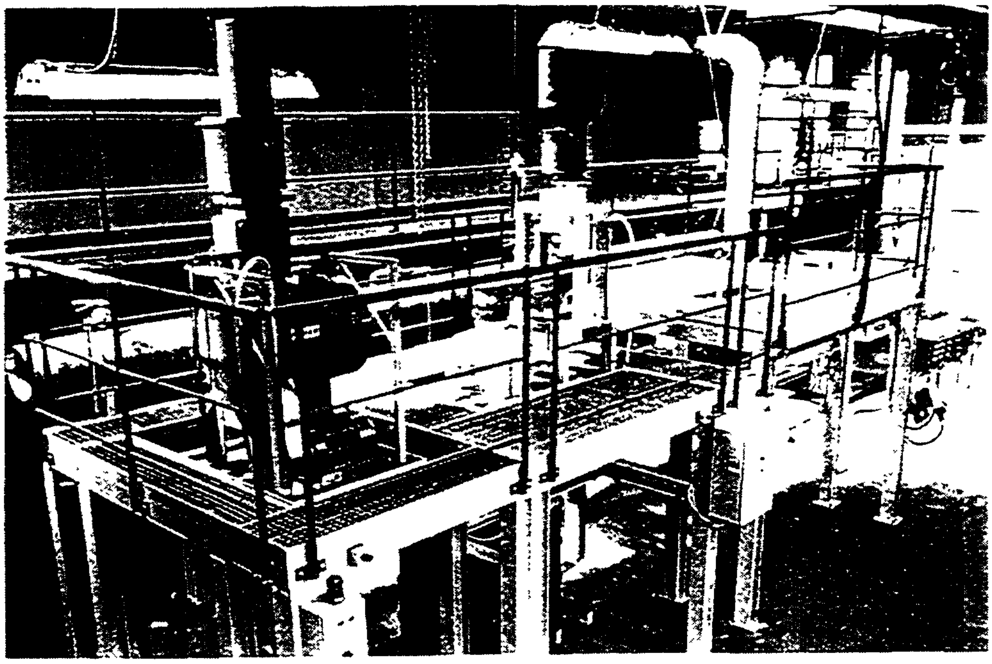


Figure V Top view of the KEMA test installation

Test-runs

The first test-runs with the installation showed that some minor modifications proved to be necessary for dust-free operation. This mainly concerned the valve construction and operation of the process containers.

Well defined, not contaminated, concrete (150 mm) cubes were made with maximum grain size of 31,5 mm. The 28 days compressive strength was about 40 N/mm^2. From the concrete composition and the sieve line of the quartz aggregate, the amount of cementstone and sand < 1 mm can be estimated. The findings are given in table IV.

It was calculated that the amount of fine material < 1 mm was 35% of the total mass of concrete. The specific mass of the concrete was taken as 2400 kg/m^3.

Test-runs were executed, in which the concrete parts were subjected to temperatures in the range of 650 - 700 °C for 3 to 4,5 hours. The milling time was set between 1 and 2 hours. After sieving over 1 mm, the amount of "clean" material proved to be 63%, and the amount of "contaminated" residue was 37% (standard deviation 3%). Because of crushing of some aggregate particles during operation, this ratio of 37% is slightly higher than the theoretical value as given in table IV.

Table IV Data of concrete mix used for the test-runs

component		amount
1	ordinary Portland Cement	320 kg/m^3
2	quartz sand < 1 mm	450 kg/m^3
3	formed cementstone (calculated)	400 kg/m^3
cementstone and sand < 1 mm (2 +3)		850 kg/m^3
fine material ratio*		35%

* (850/2400) x 100%

It can be concluded from the results that by separation, the original amount of "contaminated" concrete was reduced to 37% of the input material This corresponds with a volume reduction of about 2,5.

An impression of separated concrete samples can be got from figure VI. Material smaller than 1 mm as well as material that retained on 1 mm sieves is shown. Note the remaining dust layer on the aggregate particles (> 1 mm). During the continuation of the project this layer could be removed by wet sieving.

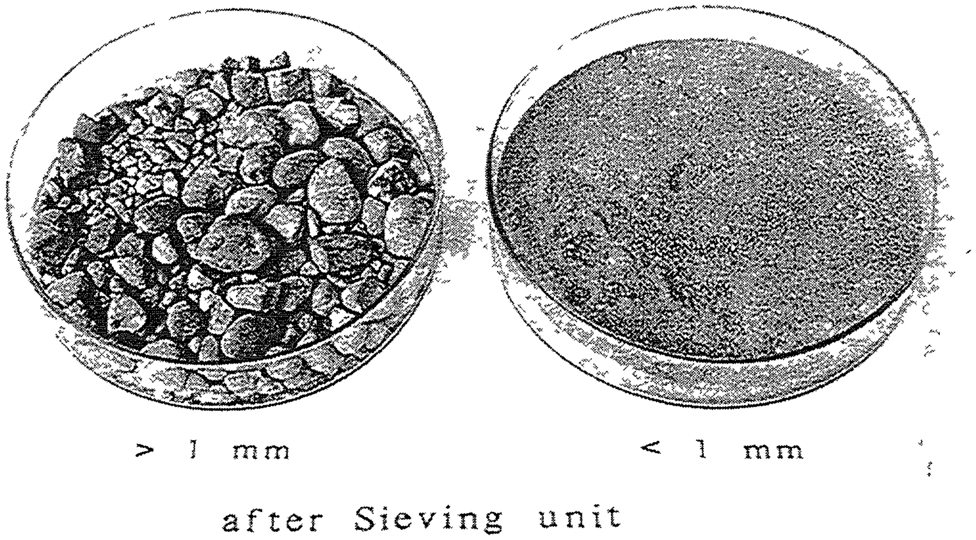


Figure VI Concrete separated in clean aggregate (> 1 mm) and contaminated fines (< 1 mm)

Separation and production of fine material

The present separation process was optimized for the production of clean aggregates (> 1 mm). A further improvement is the reduction of volume of the fine 'clean' material, quartz. In this paragraph a general description is given about the concrete separation process and the process variables which will be maintained for processing of fine material out of the concrete of CEA-UDIN and BNFL (Peeze Binkhorst, 1997).

For the research programme, the settings of process variables for processing of the different types of concrete from the nuclear facilities of CEA-UDIN and BNFL were selected:
- temperature heating 700 °C
- cooling down for 8 hours
- milling time 1 hour
- sieve size 0,5 mm and sieving time 1 hour.

Normally the process parameters have to be changed with the composition of the concrete, because these parameters effect the separation efficiency. However, the objective of this part of the project is to investigate the opportunities of the re-use of the fine ('rad waste') material of < 1,0 and material < 0,5 mm.

For the study of the separation of quartz (SiO_2) from the fine material (being cementstone plus quartz), a start was made by the production of 85 kg of fine material < 1.0 mm out of 245 kg concrete available at KEMA. After that KEMA received 170 kg of inactive concrete core samples, taken out of the Sea Tank Building located at Sellafield, from BNFL. This concrete was also processed in the separation installation of KEMA. The material was sieved over sieve 0.5 mm, see table V. The material < 0.5 mm contains cementstone agglomerates and quartz. The material > 0.5 mm was sieved over sieve 1.0 mm. As proved before, this aggregate > 1.0 mm mainly contains quartz.

Table V Results separation concrete BNFL

concrete BNFL	run 1	run 2	run 3	run 4	run 5	run 6
weight	33,094	33,589	34,164	32,941	33,976	33,713
after heating	30,491	30,930	31,636	30,493	31,415	31,220
weight loss dry (%)	8,54	8,60	7,99	8,03	8,15	7,99
after milling and sieving						
< 0,500 mm	6,353	6,359	5,908	7,034	6,707	6,182
> 0,500 mm	23,412	24,730	25,246	23,924	24,930	25,000
% < 0,500 mm	21,34	20,45	18,96	22,72	21,20	19,83
% > 0,500 mm	78,66	79,55	81,04	77,28	78,80	80,17
total	29,765	31,089	31,154	30,958	31,637	31,182
loss	0,726	-0,159	0,482	-0,465	-0,222	0,038
loss in %	2,44	-0,51	1,55	-1,50	-0,70	0,12

note: weight in grams

Electrostatic separation

Electrostatic separation of particles also called "high voltage separation" is a separation method which is based on the differences in polarity (positive and negative charges) of electric charged particles, influenced by an electric field. The separation condition is that the different particles should have a different electrostatic property. The result of the inventory study of CEA-UDIN showed that electrostatic separation is used in the mineral industry. KEMA experiences are based on electrostatic separating of different synthetic materials. From this point of view it was decided to focus on electrostatic separation of cement stone based on electrophoresis.

Electrophoresis is the movement of a charged particle influenced by an electrical field (figure VII).

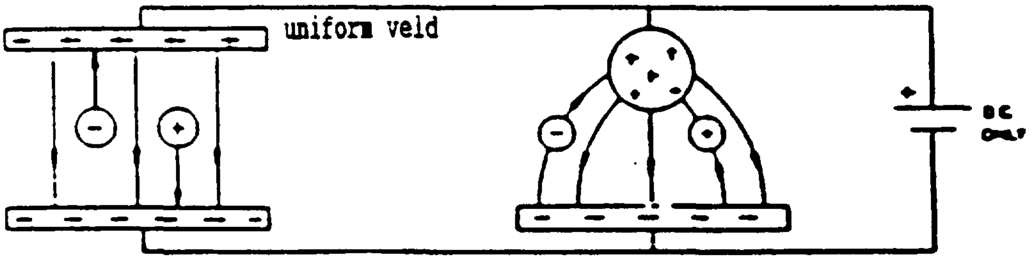


Figure VII Electrophoresis

There are three methods to charge of the particles, known by:
- corona charging
- induction charging
- contact charging.

Separation by means of a corona charging is most common. By corona charging all particles are charged with the same polarity. By moving the particle on a grounded (neutral) surface the conductive particles are neutralised and the separation can be realised between conductive and non-conductive particles.

A conductive particle which is located on a grounded plate under an electric field will be charged by the polarity of the electrode. The charged particle lifts from the surface attracted to charged electrode, Non-conductive particles are not charged.

With contact charging or piëzo charging the particles are charged by moving the particle along each other. When the particles enter a separator with a potential difference (between a negative and a positive electrode), the particles are attracted to the electrode of opposite potential.

KEMA developed and constructed a small scale electrostatic separator as shown in figure VIII. A standard electrical power supply is attached with a maximum of 30 kV. The separator has a lay out to explore the three different methods for separation as mentioned above.

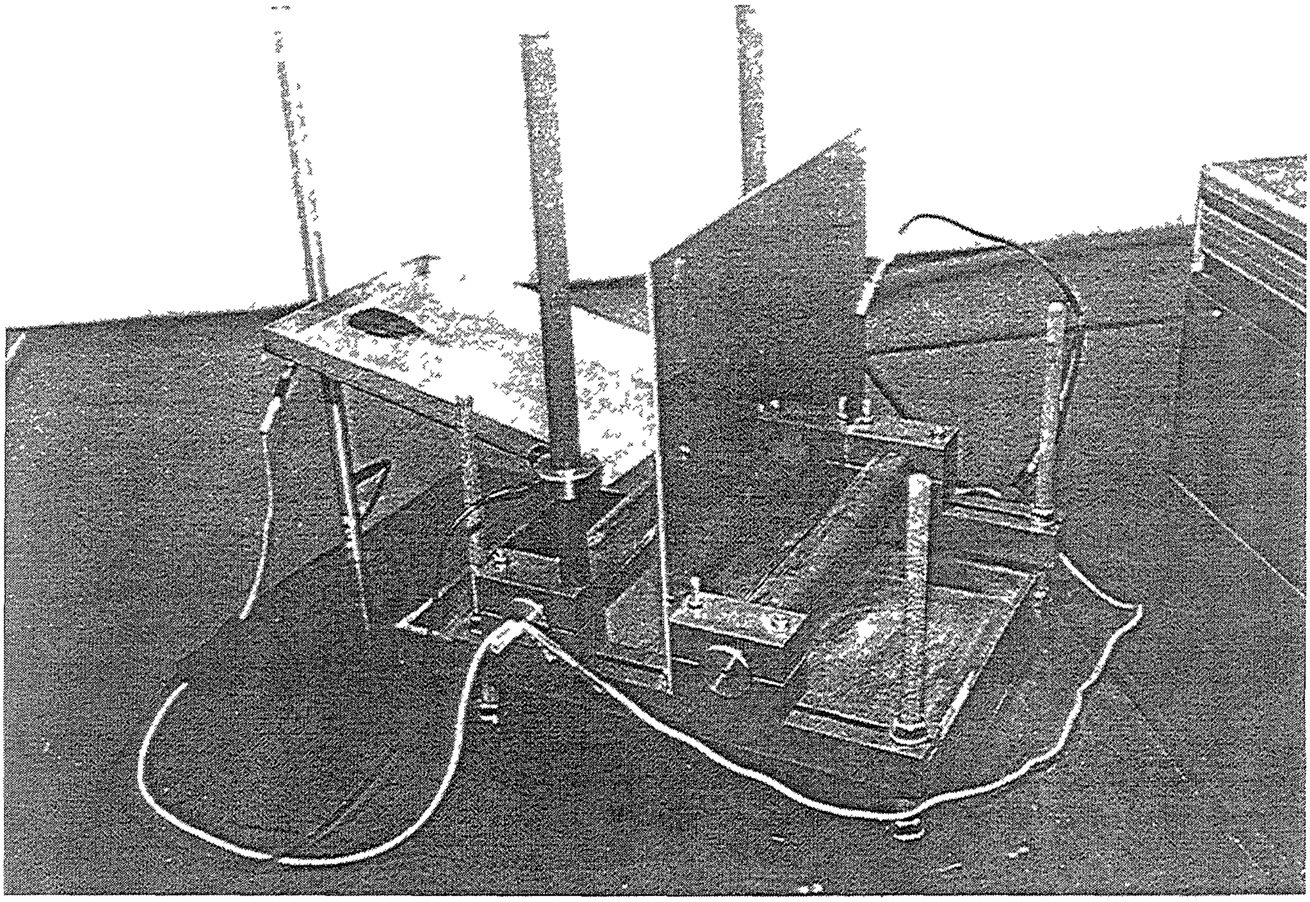


Figure VIII Small scale electrostatic separator for cementstone with quartz

ACCOMPLISHMENTS

The experiments are performed to assess the necessary parameters, to confirm the separation method and to verify the separation possibilities. The fine material (cement stone) used for electrostatic separation is processed in the KEMA separation installation and has been provided by BNFL.

An indication and the planning for the next series of experiments with material like pure sand and cement also different process parameters (corona string, grounded surface and different electrodes) are examined such as:
1 non-charged fine material
2 charged fine material by contact charging (minimal shaken)
3 fine materials charged on a grounded plate
4 non-charged fine material on an isolated grounded plate
5 negative and positive electrodes changed
6 lay out static separator: a plate and one roll charged negative and positive
7 lay out static separator: two rolls charged negative and positive
8 lay out static separator: a roll and feeder charged negative and a roll positive
9 lay out static separator: with corona string
10 lay out static separator: without corona string.

During the tests it was observed that:

- a high voltage increases the rebound of material against the (plate) electrode
- cement is attracted to negative charged electrode

- the corona string is not affective
- the minimal "shaken" material (for contact charging) is charged insufficient. It is also possible that the particles loose their charge in a humid environment.

It was shown from the results and observations of separation with corona charging (ion bombardment) and conductive charging, that these two are not a real option for further investigations. A small range in the granulometry improves the separation of different particles (cement stone and quartz) on specific gravity (density) and the dielectric value.

The observations have shown that during additional milling to break the cement stone agglomerates, the particles became static by contact charging.

Generally it can be concluded that contact charging is a favourable option. Further experiments in combination with optimisation of contact charging by milling could result in a separation (efficiency) of the quartz and the cement from fine material.

The current knowledge of inadequate for prediction of the charging of cement stone and quartz particles. Industrial implementation is necessary to assess the influence of the humidity, temperature and the size of the electric field (the polarity) and the extend of the charge.

5 SUMMARY AND CONCLUSIONS

Contamination of concrete is mainly concentrated in the porous cementstone and not in the dense aggregates like quartz gravel and limestone.

Depending on the concrete composition, volume reduction of at least a factor 2, and sometimes a factor 4, can be reached of material that has to be treated and stored as radioactive waste.

Concrete can be separated in contaminated and clean parts by means of a process based on heating, milling and sieving over 0.5 - 1 mm. The KEMA test installation showed that separation is feasible on small scale. Full scale concrete separation seems beneficial for economical and environmental reasons.

The aggregate is clean and can be re-used, whereas the cementstone can be solidified with only minor volume increase. A better option is to use this cementstone as a binder. Therefore the contaminated cementstone must be separated to enable its use as binder for concrete in the nuclear industry. This separation technology needs further optimization.

By volume reduction of contaminated concrete and re-use of the residues, a considerable contribution can be given to environmentally and economically sound assessment of the consequences of nuclear power generation up to decommissioning.

BIBLIOGRAPHY

CORNELISSEN, H.A.W., "Test Installation for Volume Reduction of Contaminated/Activated Concrete," KEMA-report 40913-KET/R&B 95-4078, September 1995.

PEEZE BINKHORST, I.A.G.M., "Rebondin Intermediate Report part 1 and part 2," KEMA-report 00332-KST/MAT 97-6632, November 1997.

DEVELOPMENT OF NEW CHEMICAL AND ELECTROCHEMICAL DECONTAMINATION METHODS FOR SELECTED EQUIPMENT OF WWER-440 AND WWER-1000 REACTOR PRIMARY CIRCUIT

M. SOLČÁNYI, D. MAJERSKÝ
Decontamination Development and Realization Centre,
Jaslovske Bohunice, Slovakia

Abstract

Special devices for in-situ application of decontamination technologies assigned for Steam Generator, Pressurizer and Main Circulating Casing of VVER-1000 type were designed, manufactured and tested in real conditions of their use in above Primary Circuit components

New decontamination technologies like low-concentration process NP-NHN for the decontamination of the Steam Generator, combined chemico-mechanical treatment for the Pressurizer and semi-dry electrolysis for the Main Circulating Pump Casing were developed and approved for their safe plant application from point of view of decontamination efficiency, corrosion influence and processing of secondary wastes

Main technological parameters were defined to achieve high decontamination efficiency and corrosion-safe application of all decontamination technologies.

1. INTRODUCTION

In 1993, AllDeco gained a contract from the NPP in Temelín (Czech Republic) for the delivery of the complete decontamination technologies, including appropriate application devices designed for the in-situ decontamination of main components of the primary circuit of the VVER-1000 type i e Steam Generator (SG), Pressurizer and Main Circulating Pump (MCP)

Appropriate decontamination technologies for the application in the NPP in Temelín were selected on the base of extensive development and application experience of research and realization workers of AllDeco in the area of in-situ as well as bath chemical and electrochemical decontamination of similar components of the primary circuit of the VVER-440 type in Jaslovské Bohunice (Slovak Republic) and Dukovany (Czech Republic)

New decontamination technologies were verified in large-scale laboratory and plant tests and finally, they were approved for their safe plant application from point of view of decontamination efficiency, corrosion influence and processing of secondary wastes

Simultaneously, the development, design and manufacture of appropriate application devices were in progress as a part of the complex technological solution of the decontamination techniques for SG, Pressurizer and MCP Casing

This Final Report is the part of the Research Project **"Development of New Chemical and Electrochemical Decontamination Methods for Selected Equipments of VVER-440 and VVER-1000 Types Reactor Primary Circuit"** being defined in the frame of the **Co-ordinated Research Programme on Optimization of Decontamination for Maintenance and Decommissioning (1994-1998)** and realized under the **Research Contracts No.: 7967/RB, 7967/R1/RB and 7967/R2/RB**

In this Final Report, there is a short overview of all main topics being performed and summarized are results from the 3-year progress of the development and project study of special decontamination techniques for main components of the Primary Circuit of VVER-1000 type All details can be found in corresponding Progress Reports [1, 2, 3]

2. PROJECT DEFINITION

Following objectives of the research project were stated and realized

- Development of a low-concentration decontamination redox process for the SG of the VVER-1000 type,
- Development of a combined chemical and chemico-mechanical decontamination process for the Pressurizer of the VVER-1000 type,

- Development of the semi-dry electrolysis for the MCP Casing of the VVER-1000 type;
- Development, design and manufacture of appropriate means for in-situ application of above decontamination technologies;
- Large-scale corrosion and metallographic tests of all decontamination methods;
- Evaluation of secondary radioactive wastes processing;

3. REALIZATION OF THE RESEARCH PROJECT

The realization of the Research Project was performed in 3 subsequent years with the analysis of initial conditions at the beginning and with the manufacture of application devices at the end of this period.

3.1 Characteristics of equipments to be decontaminated

The NPP in Temelín is represented by 2 blocks equipped with light-water reactor (PWR) of the VVER-1000 type (Russian design) of rated electrical power output 981 MWe per block.

There are 4 cooling loops in the primary circuit operating at the pressure of 15.7 MPa and coolant temperature of 290 °C (input) or 322 °C (output) with the coolant flow rate of 84 000 $m^3.hour^{-1}$. Each loop is equipped with 1 horizontal SG with the primary side internal volume of heat-transfer tubes and headers of 20 m^3. In each cold leg, there is 1 MCP with the output of 21 000 $m^3.hour^{-1}$; height of MCP Casing is 2 800 mm, min. diameter 810 mm and max. diameter 1 200 mm. In one of cooling loops a Pressurizer (Volume Control Tank) is placed with an internal diameter of 3 000 mm and height of 12 900 mm.

All above components of the primary circuit were manufactured by the Company Vítkovice, a.s. (CR) and they were made of austenitic, titanium stabilized stainless steels of 17.246 or 17.247 type (Czech Standard) that are similar to original Russian steels of 08Ch18N10T type with average contents of Cr(18%) and Ni(8%).

3.2 Characteristics of primary circuit internal corrosion layers

Contaminated corrosion layers on primary circuit internal surfaces of the NPP of PWR type are characteristic with the presence of the compact corrosion layers adhering to the base metal formed by mixed oxides of the substituted magnetite type with relatively high chromium content and outer, less fixed layers formed by partly separated crystals of oxides with high content of iron.

Contaminated corrosion layers of this kind were found on different surfaces from the PWR primary circuit of the NPPs of the VVER-440 type.

Single crystals or their aggregates mostly formed by magnetite with high content of iron are relatively easy to remove by mechanical or chemical treatment. This outer layer contains 6 - 8 % of total surface contamination as it was found, e.g. by comparison of activities of simple swabs and electrochemical samples taken from various areas on inner surfaces of the Pressurizes in the NPP V-2 (VVER-440) in Jaslovské Bohunice.

Under the porous outer layer a partly amorphous sublayer can be found. This inner corrosion layer is chromium enriched and stable against chemical treatment. The inner corrosion layer grows following crystallic structure of the base metal and the corrosion rate is faster on grain boundaries.

Character and properties of these corrosion layers considerably affect selection of processes and application conditions that would be efficient enough for removal contaminated layers during decontamination.

3.3 Selection of appropriate decontamination methods

Basic requirements of the NP in Temelín on decontamination technologies for selected components of the primary circuit were following:

a) minimization of radioactive wastes production and their processability;

b) achievement of required reduction of non-fixed surface contamination (<37 $Bq.cm^{-2}$) and reduction of dose rates;

c) acceptable corrosion influence of decontamination technologies on the equipment being treated;

These parameters were qualitatively and quantitatively compared with results achieved using decontamination processes from the original project based on concentrated oxidation-reduction solutions (AP-Citrox(20/20) as well as with results from operational decontaminations in the NPP in Dukovany (VVER-440).

Taking into account basic requirements of the NPP in Temelín put on the decontamination of selected components of the primary circuit and on the base of our experience, knowledge and results we have achieved during decontamination works performed in the NPPs in Dukovany and Jaslovské Bohunice, following decontamination technologies were selected.

3.3.1 Decontamination of the Steam Generator

A two-stage, oxidation-reduction process AP (alternatively NP)-NHN has been developed for the decontamination of the SG. This process is based on the oxidation effect of the AP solution (10 $g.dm^{-3}$ NaOH + 4 $g.dm^{-3}$ $KMnO_4$) lasting 6 hours at the temperature 90 °C and on successive action of the reduction solution NHN (mixture of an inorganic acid, reduction and complexing agents with total concentration up to 15 $g.dm^{-3}$) lasting 3 hours at the temperature 90 °C.

As the alternative to the AP solution, the oxidation solution NP (HNO_3 + $KMnO_4$ with total concentration up to 3.5 $g.dm^{-3}$) lasting 6 hour at the temperature 90 °C is considered, too.

3.3.2 Decontamination of the Pressurizer

With regard to the total volume and character of inner surfaces of the Pressurizer, a combined, chemico-mechanical decontamination method has been proposed.

a) The chemical oxidation-reduction process AP(NP)-NHN based on an oxidation effect of the AP solution (total concentration up to 14 $g.dm^{-3}$, 6 hours, 90 °C) and the reduction action of the NHN solution (total concentration 1 - 4.5 $g.dm^{-3}$, 3 hours, 90 °C) has been chosen for the bottom part of the Pressurizer (about 1/3 of the total inner volume).

   As the alternative to the AP solution, the oxidation solution NP (total concentration 1.5 - 2.5 $g.dm^{-3}$, 6 hours, 90 °C) can be used.

b) The chemico-mechanical process based on the application of a decontamination gel of GD type on the inner surface was chosen for the upper part of the Pressurizer. After 24-hour gel action, the inner surface of the Pressurizer will be finally treated using high-pressure-water jetting (water pressure up to 8 MPa).

3.3.3 Decontamination of the Main Circulating Pump Casing

Considering the additional requirement of the NPP in Temelín: metallic blank surface of the MCP Casing is to be achieved, and with regard of geometric simplicity of the MCP Casing inner surfaces to be treated, the process based on the semi-dry electrolysis has been selected. This method is based on the anodic treatment of the metallic surface using a movable electrode - cathode equipped with the swab continuously supplied wit the electrolyte solution.

The pH-neutral electrolyte is composed of salts of organic and inorganic acids and does not contain any oxalic acid or oxalates, respectively. The electrolyte composition allows using wide range of current densities (0.05 - 0.5 $A.cm^{-2}$ without any unfavorable specific corrosion attack of the base metal.

3.4 Evaluation of long-term corrosion tests

An extensive program for complex study of corrosion effects of decontamination methods being selected for the SG, Pressurizer and MCP casing of the VVER-1000 type was performed. In frame of this program wide spectrum of qualitative and quantitative parameters were evaluated that cover all important aspects concerning general as well as specific and local corrosion effects, lasting changes of mechanical properties and surface corrosion resistance as a consequence of the decontamination treatment.

All corrosion tests and their evaluation were realized in an independent, authorized institute "Divize Vítkovice Technika" in the Czech republic. Company Vítkovice a.s. is the manufacturer of the SG and Pressurizer of VVER-1000 type and of basic construction materials for other components of the primary circuit of the NPP in Temelín.

3.4.1 Specification of materials being tested

Real construction materials that will contact decontamination solutions were subjected to wide range of corrosion tests to confirm safe application of decontamination processes being developed Samples for corrosion tests were made of

- austenitic, titanium stabilized stainless steel 08Ch18N10T (as received, annealing sensitized, low-temperature sensitized, after cold deformation),
- niobium stabilized weld deposit 04Ch20N10G2B or 08Ch19N10G2B,
- isolated δ-ferrite,

3.4.2 Corrosion tests

Experimental observations were divided into two main phases In frame of the 1st phase, direct corrosion effects of decontamination processes on construction materials were evaluated The 2nd phase was aimed to the qualification of eventual effects of decontamination processes on resulting corrosion resistance of construction materials being treated

The standard process AP-Citrox was used in parallel corrosion tests for relative qualification and quantification of corrosion effects

Following corrosion tests were involved

Direct corrosion effects of decontamination:

- general corrosion rate (material loss per 1 decontamination cycle),
- metallographic and fractographic evaluation of selective corrosion effects (local corrosion attacks),

Material samples were treated in 7 decontamination cycles or in 3 initial decontamination cycles followed by 3 cycles consisting of the autoclave exposition (500 hours) and the decontamination treatment

Effects on resulting corrosion resistance after the decontamination:

- multiple oxidation in high-temperature water (HTW) in autoclaves followed by the decontamination treatment,
- sensitivity to the corrosion cracking (evaluation of initiation and spreading of tension processes, exposition of samples under mechanical tension, static loaded specimens with a crack generated),
- resistance to the pitting and crevice corrosion,
- changes in the reactivity of the surfaces (analysis of the base material surface layers, study of oxide layers formation, study of redox processes rate alteration on surfaces being decontaminated),
- stability of minority phases,
- chemical and phase analysis,

3.4.3 Results from corrosion tests

Detailed summary of results from large-scale corrosion tests represents a comprehensive report [4] (over 100 pages with 117 figures and 11 tables)

These corrosion tests and plant verifications confirm suitability of all new decontamination processes for their safe and effective use in applications they have been developed for and these technologies are approved for their routine use in the NPPs

4. DEVELOPMENT AND DESIGN OF APPLICATION DEVICES

In the frame of the complex technological solution of the decontamination techniques for the Steam Generator (SG), Pressurizer and Main Circulating Pump (MCP) Casing for the NPP in Temelín, special application devices were designed, manufactured and tested in real condition of the use for above Primary Circuit components These are

DEZA PG-1000 - application device for the SG;
DEZA KO-1000 - application device for the Pressurizer,
DEZA HCČ-1000 - application device for the MCP Casing;

A common, very important criterion for all application devices was their reliability in long-term and heavy-duty operation

Decontamination devices had to be made of materials compatible with materials of corresponding Primary Circuit components (composition, corrosion characteristics, surface finishing) and resistant to the decontamination media in heavy operation conditions

To meet all operation criteria put on the application devices it was necessary to test them in conditions as close to the operational reality as possible From this point of view, simultaneously with the application devices, testing and training stands were designed and manufactured that were assigned to tests and adjustment of corresponding devices and training of the staff to become familiar with correct handling and servicing.

All above decontamination devices allow to achieve optimal conditions of the application of corresponding decontamination technologies and the design takes into account specificity of the concrete equipment being decontaminated as well as specificity of the VVER-1000 type Primary Circuit (e.g. absence of Main Gate Valves)

4.1 DEZA PG-1000

The decontamination device DEZA PG-1000 (Fig. 1, Fig. 2 in Graphic Inset) is assigned to the application of the two-stage technology of the chemical decontamination named AP(NP)-NHN in the SG in the VVER-1000 type Primary Circuit [5]

The decontamination device DEZA PG-1000 was tested in four full decontamination cycles in the special stand and this time, it is prepared for the 5th "dry" loading into the real SG in the NPP in Temelín.

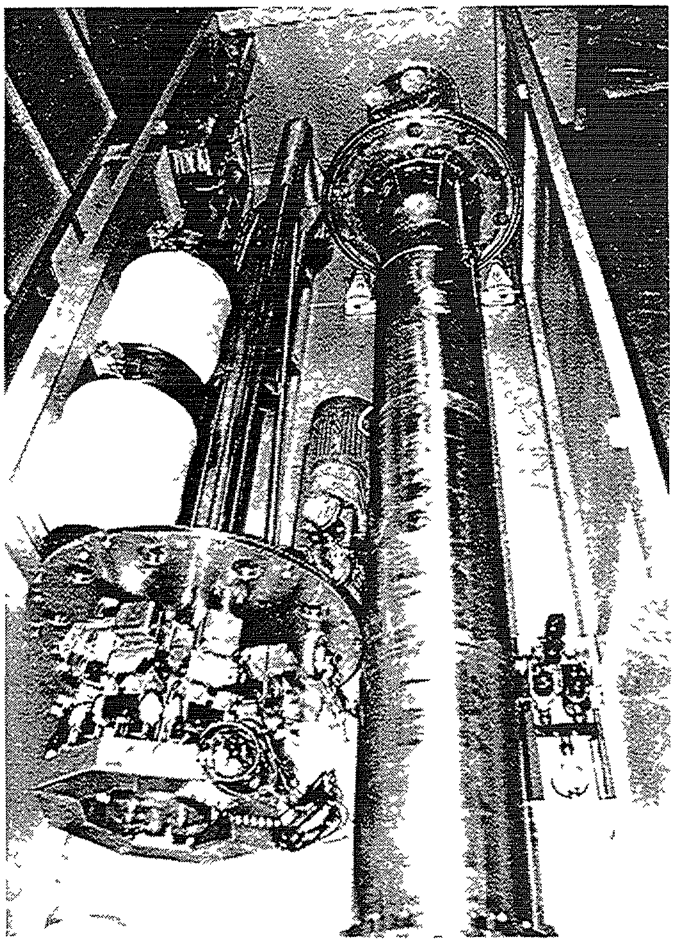


Fig. 1: DEZA PG-1000 - Circulation Unit and Control Unit in the Transport Container

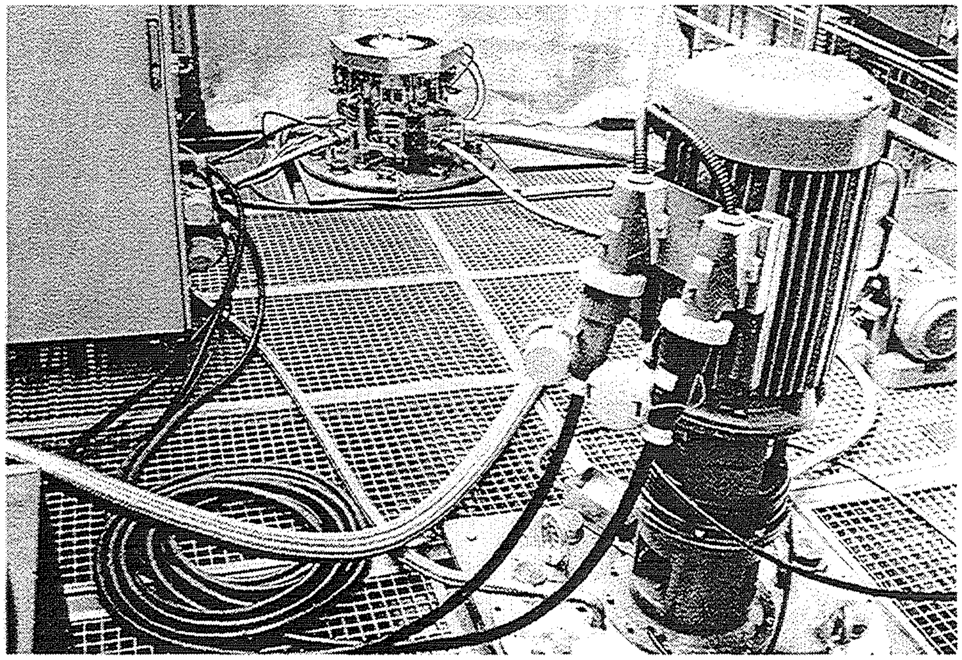


Fig. 2: DEZA PG-1000 - Circulation unit and Control unit loaded in the headers of the Stand

Decontamination equipment DEZA PG-1000 consists of following basic parts:

1. control unit (positioned into the cold SG header);
2. circulation unit (positioned into the hot SG header);
3. control station;
4. connecting hoses;
5. connecting cables;
6. auxiliary dosage pump;
7. auxiliary drainage pump;
8. accessories;
9. transport and storage container;

The **Control Unit** of the DEZA PG-1000 ensures filling of decontamination solutions into the SG, discharge of decontamination solutions from the SG, enables operational sampling and correction of chemical characteristics of decontamination solutions (pH, concentration) by dosage of concentrates of reagents. Control unit also holds sensors for monitoring of liquids (level, temperature) in the SG in different stages of the decontamination.

The **Circulation Unit** of the DEZA PG-1000 ensures circulation of decontamination solutions and uniform *distribution in heat-exchanger tubes between the hot and cold headers in the SG.*

The **Control Station** enables monitoring of the level and temperature of decontamination solutions in the SG, remote control of the circulation pump, auxiliary drainage and dosage pump, filling, discharge and blow-off valves.

Flexible metallic **Connecting hoses** are made of stainless steel and they are assigned to transfer of the liquid media used for the decontamination of the SG (filling, drainage, dosage, blowing-off).

The **Connecting cables** are used for the power supply of electrical appliances and for signal transfer from sensors held by the Control unit to indicators in the Control station.

The **Auxiliary Dosage Pump** is of a plunger type and it is used for an additional dosage of concentrates of basic reagents into the decontamination solutions in the SG when the effective concentration falls below an acceptable limit.

The **Auxiliary Drainage Pump** is of a centrifugal type and it is used as a main device of the discharge system.

4.2 DEZA KO-1000

The decontamination device DEZA KO-1000 (Fig 3 Fig 4 in Graphic Inset) is assigned to the realization of the two-stage technology of the chemical decontamination named AP(NP)-NHN in the bottom part of the Pressurizer and combined chemico-mechanical decontamination in the top part of the Pressurizer in the VVER-1000 type Primary Circuit [6]

The decontamination device DEZA KO-1000 was tested in four full decontamination cycles in the special stand and this time it is prepared for the 5th "dry" loading into the real Pressurizer in the NPP in Temelin

Decontamination equipment DEZA KO-1000 consists of following basic parts

1. basic supporting column (in 5 parts),
2. sealing plug
3. carriage in transport and stabilization cage holding adjustable arms with application tools
4. section for airless decontamination gel application
5. section for high-pressure-water jetting,
6. connection and distribution frame,
7. control station
8. connecting hoses
9. connecting cables
10. accessories,
11. transport and storage container

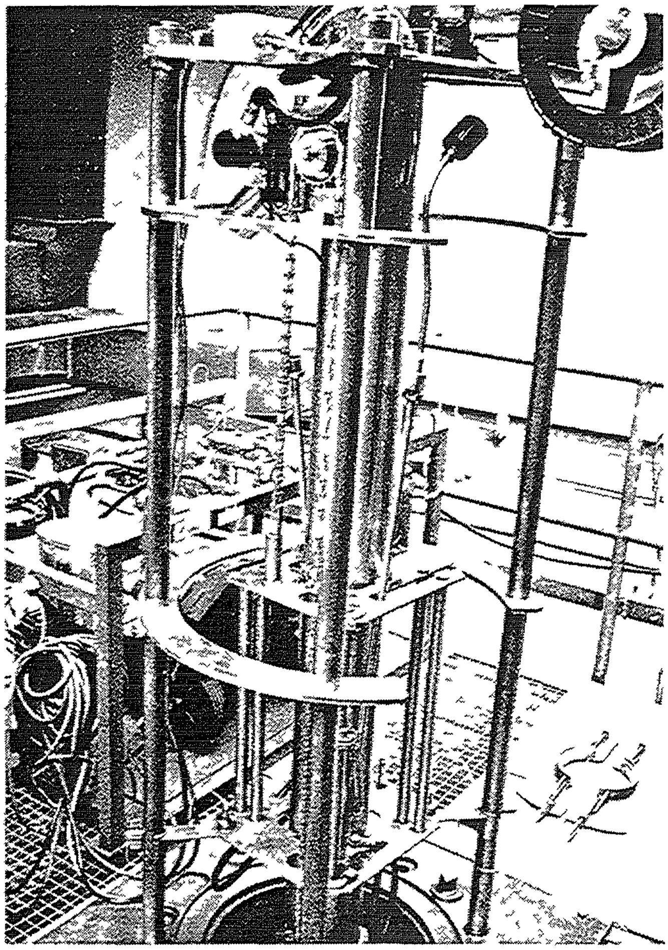


Fig. 3: DEZA KO-1000 - Carriage with Adjustable Arms in the Stabilization Cage

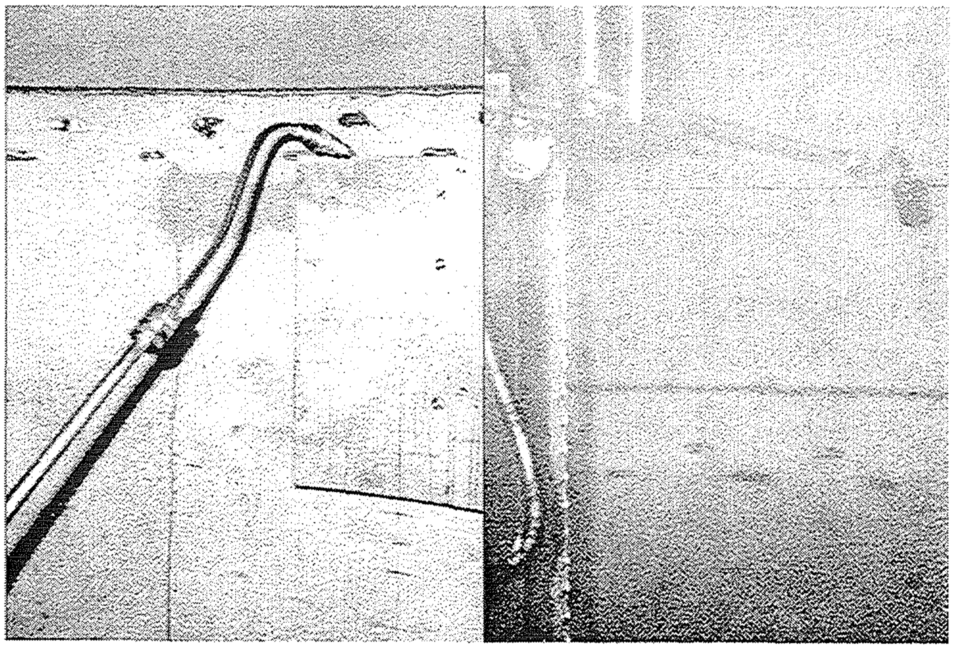


Fig. 4: DEZA KO-1000 - Decontamination Gel Application and High-Pressure-Water Jetting

The basic **Supporting Column** of the decontamination device DEZA KO-1000 ensures filling and discharge of decontamination solutions being used for the decontamination of the bottom part (1/3 of total inner volume) of the Pressurizer in the 1st stage of the decontamination.

In the 2nd stage of the decontamination of the top part of the Pressurizer (2/3 of total inner volume) the **Supporting Column** enables vertical and horizontal movement and positioning of the carriage.

The **Sealing Plug** is mounted on the lowest part of the supporting column and it ensures the reliable separation of the inner volume of the Pressurizer from the rest of the Primary Circulation Loop.

The **Carriage** is carrying adjustable arms with special jets for airless gel application and high-pressure-water jetting. The adjustable arms and jets are exchangeable to ensure their optimum working position in different cross-sections of the Pressurizer. The carriage is normally put and fixed in the transport and stabilization cage for simple and safe handling.

The **Section for Airless Gel Application** is built-up of the reservoir of the decontamination gel, high-pressure piston pump (up to 1.8 MPa) and high-pressure feeding hoses up to sockets on the carriage.

The **Section for High-Pressure-Water Jetting** is built-up of the high-pressure water pump (up to 21 MPa) and high-pressure feeding hoses up to sockets on the carriage.

Both above section are mounted into the common **Connection and Distribution Frame** with valves and piping for correct distribution of decontamination media to the working tools.

The **Control Station** enables monitoring of the pressure in the Pressurizer during the 1st decontamination stage and remote and programmable control of the carriage movement and positioning in both vertical and horizontal direction during the 2nd decontamination stage.

Flexible metallic **Connecting hoses** are assigned to transfer of the liquid media used for the decontamination of the Pressurizer (filling, drainage).

The **Connecting cables** are used for the power supply of the control station and for signal transfer from sensors on the supporting column to indicators in the Control station.

4.3 DEZA HCČ-1000

The decontamination device DEZA HCČ-1000 (Fig. 5, Fig. 6 in Graphic Inset) is assigned to the application of the semi-dry electrochemical decontamination in the MCP Casing in the VVER-1000 type Primary Circuit [7].

This device has to enable proper separation of the MCP Casing from the rest of the circulation loop, precise positioning of working tools, controlled distribution of the electrolyte and operating current into the electrodes, final water rinsing and discharge of the spent liquid media.

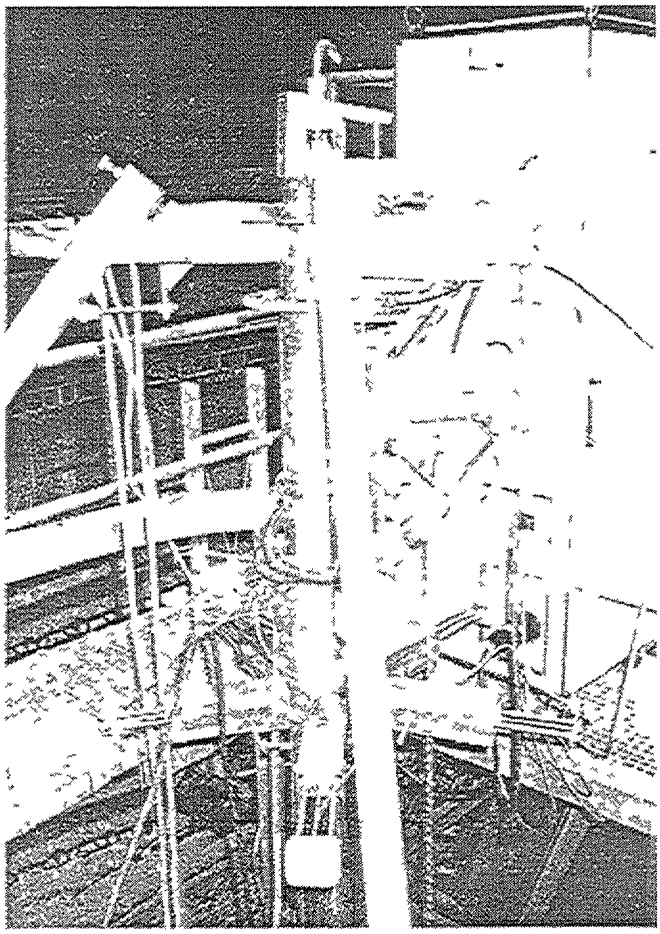


Fig. 5: DEZA HCČ-1000 - Supporting Column with the Carriage in the Upper Position

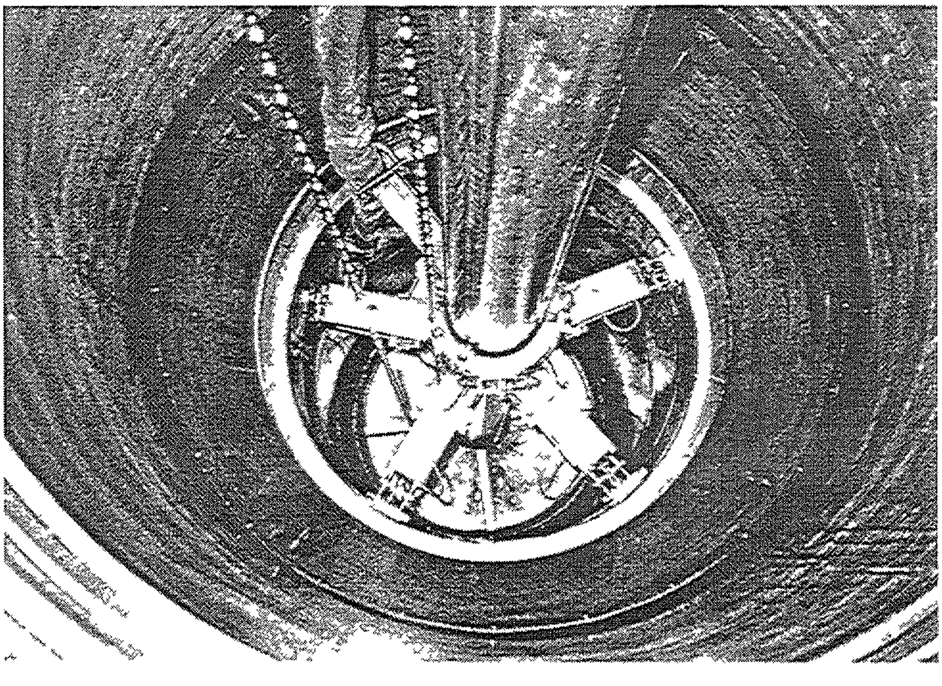


Fig. 6: DEZA HCČ-1000 - Electrodes in the Working Position

The decontamination device DEZA HCČ-1000 was tested in four full decontamination cycles in the special stand and in the additional 5th "dry" loading into the real MCP Casing in the NPP in Temelin

Decontamination equipment DEZA HCČ-1000 consists of following basic parts

1. basic supporting column,
2. sealing plug with the spent electrolyte collector,
3. carriage with the set of working tools,
4. *section for electrolyte and rinsing water supply,*
5. rectifier,
6. pneumatic unit,
7. control station,
8. connecting hoses,
9. connecting cables,
10. accessories,
11. transport and storage container,

The basic **Supporting Column** of the decontamination device DEZA HCČ-1000 enables vertical and horizontal movement and positioning of the carriage in different heights and cross-sections of the MCP Casing

The **Sealing Plug** is mounted on the lowest part of the supporting column and it ensures the reliable separation of the inner space of the MCP Casing from the rest of the Primary Circulation Loop and it holds the collector of the spent electrolyte

The **Carriage** is carrying adjustable, pneumatic arms with 4 special-shaped electrodes and 1 rinsing jet The system of adjustable arms allows the working electrodes to reach diameters from 810 mm to 1200 mm Special-shaped electrodes wearing swaps are exchangeable to ensure optimum treatment of different surfaces in the MCP Casing

The **Section for Electrolyte and Rinsing Water Supply** is built-up of a reservoir for the electrolyte and the second one for the rinsing water with a pumping system using pressurized air

The **Rectifier** is a source of the direct current for the electrolysis with the current limit set to 50 A and the voltage limit of 30 V

The **Pneumatic Unit** allows control and positioning of adjustable pneumatic arms, pumping of the electrolyte and rinsing water into the working tools and regular discharge of the collector of the spent electrolyte

The **Control Station** enables programming, control and monitoring of movements and working positions of the carriage and parameters of the electrolysis

The **Connecting hoses** are assigned to transfer of the liquid media used for the decontamination of the MCP Casing (feeding, discharge)

The **Connecting cables** are used for the power supply of the control station, electrical appliances and working electrodes and for signal transfer from sensors on the supporting column to indicators in the Control station

5. SECONDARY RADIOACTIVE WASTES - BALANCE

New decontamination formulations developed for the SG, Pressurizer and MCP Casing of the Primary Circuit in the NPP in Temelín are based on the use of the liquid media containing various active chemical agents to achieve effective and safe decontamination and low production of secondary radioactive wastes

The decontamination of the SG will be performed using the chemical, two-stage, oxidation-reduction process based on a basic oxidation solution of AP type and a reduction solution of NHN type As an alternative an oxidation solution of the NP type may be used in the oxidation stage

The decontamination solutions for the treatment of the bottom part of the Pressurizer are of the same type as those ones used for the SG, Upper part of the Pressurizer will be decontaminated using special decontamination gel and subsequent high-pressure-water jetting

The MCP Casing decontamination will be performed using the technology of semi-dry electrolysis

Basic composition of above decontamination media are shown in the Table 1.

Table 2 shows expected amounts of spent decontamination solutions and the balance of secondary radioactive wastes from the decontamination of above equipments in 1 year period:

1 SG - 2 decontamination cycles;
1 Pressurizer - 1 decontamination cycle;
1 MCP Casing - 1 decontamination cycle;

Table 1: *Basic chemical composition of decontamination solutions for the SG, Pressurizer and MCP Casing treatment*

Decontamination method	Stage (total concentration / g.dm^{-3})	Basic components
AP-NHN for the SG	AP-oxidation (14)	$KMnO_4$ NaOH
	NHN-reduction (15)	HNO_3 Reduction agent Complexing agent
	NP-oxidation (alternative) (3.6)	HNO_3 $KMnO_4$
AP-NHN for the Pressurizer	AP-oxidation (14)	$KMnO_4$ NaOH
	NHN-reduction (5)	HNO_3 Reduction agent Complexing agent
	Decontamination Gel (GD) (760)	Glycerol Reduction agent Complexing agent
Electrolyte for the MCP Casing	Semi-dry electrolysis (40)	$(NH_4)_2SO_4$ NH_4NO_3 Complexing agent

Table 2: Expected amounts of spent decontamination media from the SG, Pressurizer and MCP Casing treatment in 1 year period

Equipment - Solution	Volume of spent solutions [m^3]		Total concentration	Final concentration of liquid radwaste from 2 Units	Volume of the concentrate from 2 Units (salinity)
	1 Unit/1 year	2 Units/1 year	[g.dm^{-3}]	[g.dm^{-3}]	[m^3]
PG - AP	2 x 20	80 + 20 *	14		
- NHN	2 x 20	80 + 20 *	15		
- water	4 x 20	160 + 40 *	-		
		Σ **400**		7.25	14.5
KO - AP	30	60 + 40 **	14		
- NHN	30	60 + 40 **	5		
- GD	0.1	0.2	760		
- water	35	70 + 7.8 **	-		
		Σ **350**		5.86	10.3
MCPC - electrolyte	0.3	0.6	40		
- water	0.1	0.2 + 1.2 ***			
		Σ **2**		12.00	0.12
Total amounts		**750**			**25**

* - increase of the solutions volume ↗ reserve and retention in piping;
** - increase of the solutions volume ↗ reserve and consumption in decontamination baths;
*** - increase of the solutions volume ↗ rinsing water for final cleaning of decontamination devices;

6. MAIN TECHNOLOGICAL PARAMETERS

All new decontamination technologies were successfully verified in many laboratory and plant decontamination and corrosion tests and the full compatibility with construction materials of the Primary Circuit as well as materials of decontamination devices was approved

6.1 Decontamination of the Steam Generator

Real decontamination conditions:

oxidation solution - AP (14 g dm^{3})
(alternative oxidation) - NP (3 6 g dm^{3})
oxidation step - 6 hours
reduction solution - NHN (15 g dm^{3})
reduction step - 3 hours
operational temperature - 90-95 °C

6.2 Decontamination of the Pressurizer

Real decontamination conditions:

Bottom part

oxidation solution - AP (14 g dm^{3})
oxidation step - 6 hours
reduction solution - NHN (5 g dm^{3})
reduction step - 3 hours
operational temperature - 90-95 °C

Top part

decontamination gel - GD (760 g dm^{-3})
gel application time - 1 5 hour
gel reaction time - 20-24 hours
high-pressure jetting - clear water
time of one step - 2 hours
operational temperature - 30-50 °C

6.3 Decontamination of the MCP Casing

Real decontamination conditions:

electrolyte - pH=7 (40 g dm^{3})
current density - +30 A dm^{2}
treatment time - 7 5 hours

7. CONCLUSION

In frame of the Research Project new decontamination technologies were developed for selected components of the primary circuit of the VVER-1000 type

☑ Two-stage, low-concentration, oxidation-reduction decontamination process for the Steam Generator;
☑ Combined chemical and chemico-mechanical decontamination treatment for the Pressurizer;
☑ Semi-dry electrochemical decontamination technology for the Main Circulating Pump Casing,

All above decontamination technologies were tested and approved by the authorized Institute for their routine operational application in NPPs in the Slovak Republic and the Czech Republic

The Final Report also summarizes basic facts on final design, manufacture and testing of application devices for new decontamination technologies for selected components of the Primary Circuit of VVER-1000 type in the NPP in Temelín Results from the stand tests being performed have confirmed the reliability of the machinery and the reality of achieving of basic obligatory technological parameters having been defined in the initial project phase

A specialized authority evaluated contribution of radioactive wastes from the decontamination technologies application and their influence on anticipated radioactive wastes from the NPP regular operation The detailed analysis of the input data confirmed the compatibility of radioactive wastes originated from the decontamination with other radioactive wastes collected from other sources The bituminization technology as well as the cementing technology are acceptable for processing of liquid radioactive wastes from the decontamination using new formulations These processes will lead to the stable and resistant products from the fixation treatment of radioactive wastes

REFERENCES

1. M Solčányi, D Majerský **"Development of New Chemical and Electrochemical Decontamination Methods for Selected Equipments of VVER-440 and VVER-1000 types reactor Primary Circuit"**, Progress Report (May, 1994 - February, 1995), CRP on Optimization of Decontamination for Maintenance and Decommissioning, IAEA Contract No . 7967/RB, February, 1995,
2. M Solčányi, D Majerský **"Development of New Chemical and Electrochemical Decontamination Methods for Selected Equipments of VVER-440 and VVER-1000 types reactor Primary Circuit"**, Progress Report (May, 1995 - February, 1996), CRP on Optimization of Decontamination for Maintenance and Decommissioning, IAEA Contract No 7967/R1/RB, February, 1996,
3. M Solčányi, D Majerský **"Development of New Chemical and Electrochemical Decontamination Methods for Selected Equipments of VVER-440 and VVER-1000 types reactor Primary Circuit"**, Progress Report (July, 1996 - May, 1997), CRP on Optimization of Decontamination for Maintenance and Decommissioning, IAEA Contract No 7967/R2/RB, May, 1997,
4. J Bystrianský, I Lenártová **"Posouzení a zhodnocení přijatelnosti korozního působení nových dekontaminačních technologií"** (Evaluation of Acceptability of Corrosion Effects of New Decontamination Technologies), Záverečná správa, Ostrava-Vítkovice, december 1995,
5. D Majerský **"Technológia chemickej dekontaminácie parogenerátora"** (Technology for the Steam Generator Chemical Decontamination), Sprievodná správa AllDeco s r o , Jaslovské Bohunice, jún 1996,
6. D Majerský **"Technológia chemicko-mechanickej dekontaminácie kompenzátora objemu"** (Technology for the Chemico-Mechanical Decontamination of the Pressurizer), Sprievodná sprava AllDeco s r o , Jaslovské Bohunice, jún 1996,
7. M Solčányi **"Technológia polosuchej elektrochemickej dekontaminácie ulity hlavného cirkulačného čerpadla"** (Technology for the Electrochemical Decontamination of the Main Circulating Pump Casing), Sprievodná správa AllDeco s r o , Jaslovské Bohunice, jun 1996,

THEORETICAL INVESTIGATION OF ASPECTS OF RADIOACTIVE CONTAMINATION

A.H. SMITH, M.R. CHANDRATILLAKE, J.B. TAYLOR
British Nuclear Fuels plc,
United Kingdom

Abstract

The BNFL programme of work has investigated theoretical aspects of the mechanisms responsible for the deposition and adherence of contamination to metallic surfaces and the energetics of physical decontamination processes. The work has been conducted in two phases:

- The theoretical and laboratory study of deposition of species from aqueous media on to stainless steel
- Theoretical assessment of the forces causing the attraction of PuO_2 and UO_2 particles to stainless steel in an air environment and comparison of these forces with the energies delivered by physical jetting processes.

The first phase produced a model which was found to give good agreement with plant operational experience of the deposition of simple aqueous ions such as Cobalt. Due to the complexities, however, of surface / colloid and surface / particle interactions the model was found not to be successful at predicting deposition for more complex compounds, such as Ruthenium Nitrosyls. At this stage the model had fulfilled its original requirement of underpinning design work on pipework shielding systems and it was decided not to pursue the library of chemical speciation data that would be necessary to model the behaviour of a full spectrum of possible contaminants.

The second phase predicts by theoretical analysis that the relation of the energy delivered by jetting techniques to the physical forces causing the adherence of PuO_2 and UO_2 particles will vary considerably with particle size. This is particularly notably for larger PuO_2 particles which are firmly held as a result of high levels of electrostatic charge due to their intense alpha activity. Small particles tend to be difficult to remove due to the low profile that they present to the jetting medium. Large and small PuO_2 particles and small UO_2 particle are thus predicted to be difficult to remove and will present an energy threshold which may not be crossed by all decontamination techniques.

Introduction

This study addresses the theoretical assessment of the mechanisms of the contamination of stainless steel surfaces by radioactive species. This is intended to complement the more practical projects that form the basis of the present Research Group, with the aim of facilitating the selection and optimisation of decontamination processes for specific contamination scenarios. Two different types of contamination are considered; adsorption from aqueous solution and particle deposition in atmospheric air. Worked examples have concentrated on Cobalt for the aqueous solution work and Uranium and Plutonium Oxide for the particle deposition work.

Much of the work was performed by BNFL Research and Development teams, and draws upon practical plant operational experience at BNFL's Sellafield works. Experimental work has also been performed at Kings College, University of London.

Background

The initial phase of the study grew from the necessity to have a model to understand the accumulation, or plate out, of active species on pipework at the Sellafield plant to support the design of appropriate shielding. The information gathered as part of that investigation was developed into a model which assisted the understanding of the mechanisms by which radioactive cations became attached to the surfaces of process plants. The aim of the model was to identify parameters which affected the adsorption and desorption mechanisms, and hence to selectively target these to improve decontamination performance; or better, to prevent contamination in the first place.

The second phase of the study addressed the problem of accumulation of dry particles of Uranium and Plutonium to stainless steel surfaces and compares the theoretically calculated energies necessary to remove these particles with those delivered by commonly used jetting techniques.

Technical Approach

The two phases of the study were largely theoretically based. The first phase started with the derivation of a model to describe deposition of Cobalt from aqueous solution on to stainless steel. The model considers the interactions between hydrated Co^{2+} ions at a pH range of 2-14 and the Cr rich Oxide layer covering the surface of the steel. Deposition of Cobalt was also measured experimentally under laboratory conditions and these results compared to plant data relating to the accumulation of plate out of active species on pipework at the Sellafield plant.

The results of the modelling work were found to give reasonable agreement with the observed behaviour of Cobalt, but it was less successful for more complex species. It was felt at this stage that the modelling had fulfilled its original requirement of underpinning design work on pipework shielding systems. Considerable effort would be necessary to compile a library of chemical speciation data to enable the model to address a full range of likely contaminants and this was not considered worthwhile.

For this reason the second phase of the study involved a change of direction and has investigated a problem facing all decommissioners of nuclear facilities; that of deposition of Uranium and Plutonium Oxides on stainless steel surfaces. Information from the scientific literature and BNFL's own data was used to enable first principle calculation of the forces binding these particles to steel surfaces and to allow comparison of the energetics of particle removal with the energy delivered by simple jetting techniques.

Results

The following are the principal findings from the study:

- The plate out of material on to a stainless steel surface is controlled by the pH of the liquor modifying the surface potential of the surface oxide layer. This potential interacts with the charged ion or surface potential of colloids or solids.
- Plate out for ions and colloids is a non-linear function of isotopes in solution. For suspended solids this is less obvious since saturation of surfaces at specific levels for certain solids has been demonstrated.

- Once deposited it is suggested that reversible, dynamic equilibrium, chemical reactions exist at the oxide surface. Equilibrium conditions have been observed to occur (experimentally) within a matter of days.
- Stainless Steel surface damage is believed to 'capture' ions and micron size particles and influence the equilibrium by delaying the release of captured material.
- Transient conditions in pH or concentration, that occur for short periods (eg: 24 hours) should not lead to a major plate out problem. (An element of judgement is necessary here, due to the complexity of surfaces interactions to short term changes).
- The influence of liquid turbulence can be ignored.
- Currently there is no data from experiments to predict or estimate deposition of fuel fines or floc. Upper bound magnetite surface saturation data is available.
- Multi layer deposition of ions, colloids and solids has not been identified as excessive. All data presented is for equilibrium conditions which takes due account of multi-layer deposition.
- UO_2 and PuO_2 particles are held on to stainless steel surfaces by a range of physical and chemical forces.
- The removal of particles held by chemisorption require energy several orders of magnitude higher than for particles held by physical forces alone.
- For physically bound PuO_2, the image-charge force is the most significant physical force for particles above 10 microns. This is several orders of magnitude greater than that on UO_2 particles in this size range, and is due to the α-activity of the PuO_2.
- Total physical forces acting on a particle do not vary significantly with the orientation of the substrate. This is because the Van der Waals and image-charge forces, which always favour adhesion, dominate the gravitational force for the particle size range considered (up to 20 microns).
- UO_2 particles larger than 20 μm will not be deposited on a horizontal surface from below as the gravitational force on larger particles is stronger than the Van der Waals and image-charge forces. For PuO_2 particles of 20 microns, the image-charge force is significantly greater than gravity and thus these particles will be strongly adhered.
- In comparison with the energy delivered by jetting techniques, physically adsorbed PuO_2 particles show a critical intermediate size range which is easier to remove than larger or smaller particles. In the case of PuO_2, particles between approximately 0.3 and 3 microns can be removed by 15 bar water jetting at 0.5 m stand off distance, whilst larger and smaller particles will not be removed.
- Air jetting can remove only the particles adsorbed by physisorption. Particle sizes in the range of 0.1 to 2.5 μm can be removed with velocities of the order of few cm/s. Higher velocities are required for particles larger than 10 μm and also for particles smaller than 0.1 μm.
- UO_2 particles larger than 10 μm require air velocities ten to sixty times higher than those for UO_2, due to the strong image-charge forces experienced by PuO_2.

REFERENCES

1. Information on Cobalt deposition taken from J B Taylor; 1990 Thesis: A Theoretical Analysis of the Deposition of Radioactive Ions, Particles and Colloids from Aqueous Liquids on to Stainless Steel

2. Information on Uranium and Plutonium particle deposition taken from: Energetics of Contamination Mechanisms and Decontamination Techniques, J Swash, P Roper, M R Chandratillake, IAEA 1998

PARTICIPANTS IN THE CO-ORDINATED RESEARCH PROGRAMME

Binkhorst, I.P.	Environmental Technology Department, KEMA/Nederland BV, P.O. Box 9035, 6800 ET Arnhem, the Netherlands
Borioli, E.	Nuclear Energy Division, ENEL/Italian Electricity Company, Via Monfalcone 15, I-20132 Milan, Italy
Clark, D.E. *(Scientific Secretary)*	Division of Nuclear Fuel Cycle and Waste Technology, International Atomic Energy Agency, Wagramerstrasse 5, A-1400 Vienna, Austria
Cornelissen, H.A.W.	Environmental Technology Department, KEMA/Nederland BV, P.O. Box 9035, 6800 ET Arnhem, Netherlands
Costes, J.R.	Rhone Valley Nuclear Research Center/CEA, BP 171, 30207 Bagnols sur Ceze, France
Daryoko, M.	Radioactive Waste Management Technology Center (PTPLR), National Atomic Energy Agency (BATAN), Kawasan Puspiptek, Serpong, 14310 Jawa Barat, Indonesia
de Araujo, J.A.	Instituto de Pesquisas Energeticas e Nucleares, Comissao Nacional de Energia Nucleare, Cidade Universitaria Butanta, Sao Paulo, Brazil
Efremenkov, V.	Institute of Radioecological Problems, Belarus Academy of Science, 220109 Minsk, Sosny, Belarus
Klein, M.	SCK-CEN, Studiecentrum voor Kernenergie, Boeretang 200, B-2400 Mol, Belgium
Krasznai, J.	Ontario Hydro Technologies, 800 Kipling Avenue, Toronto, Ontario, M8Z 5S4 Canada
Makai, J.	Paks Nuclear Power Plant Ltd., P.O. Box 71, H-7031 Paks, Hungary
Moorthy, J.N.	Applied Chemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai (Bombay) 400 085 India
Ren, X.W.	China Institute for Radiation Protection, P.O. Box 120, Taiyuan, Shanxi 030006, China
Rezbarik, J.	Decontamination Development and Realization Centre, All Deco s.r.o., 919 31 Jaslovske Bohunice, Slovakia

Schunk, J.	Paks Nuclear Power Plant Ltd., P.O. Box 71, H-7031 Paks, Hungary
Smith, A.H.	British Nuclear Fuels plc, UK Group Sellafield, B229 Seascale, Cumbria, CA20 1HL, United Kingdom
Solcanyi, M.	Decontamination Development and Realization Centre, All Deco s.r.o., 919 31 Jaslovske Bohunice, Slovakia
Steinwarz, W.	Siempelkamp Giesserei GmbH, Siemplekampstrasse 45, D-47803 Krefeld, Germany
Taylor, J.B.	British Nuclear Fuels plc, Risley, Warrington, Cheshire, WA4 6AS, United Kingdom
Voronik, N.	Institute of Radioecological Problems, Belarus Academy of Science, 220109 Minsk, Sosny, Belarus
Wiley, J. *(Scientific Secretary)*	Division of Nuclear Fuel Cycle and Waste Technology, International Atomic Energy Agency, Wagramerstrasse 5, A-400 Vienna, Austria
Yatim, S.	Radioactive Waste Management Technology Center (PTPLR), National Atomic Energy Agency (BATAN), Kawasan Puspiptek, Serpong, 14310 Jawa Barat, Indonesia

First Research Co-ordination Meeting, Vienna, Austria,
31 October – 4 November 1994

Second Research Co-ordination Meeting, Bombay (Mumbai), India,
26 February – 1 March 1996

Third Research Co-ordination Meeting, Mol, Belgium,
12–16 January 1998