KfK 4190
April 1987

Neue Entwicklungen auf dem Gebiet der Wiederaufarbeitung

Ausgewählte Beiträge zu einem Seminar, veranstaltet von der Gesellschaft Deutscher Chemiker (Fachgruppe Nuklearchemie), dem Verein Österreichischer Chemiker und dem Institut für Heiße Chemie des Kernforschungszentrums Karlsruhe vom 3. - 10. März 1984 in Obertraun/Österreich

Institut für Heiße Chemie
Projekt Wiederaufarbeitung und Abfallbehandlung

Kernforschungszentrum Karlsruhe

KERNFORSCHUNGSZENTRUM KARLSRUHE

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Kernforschungszentrum Karlsruhe GmbH, Karlsruhe

CONTENTS

1. K. Eiben, H. Zimmermann:
   Uranium Extraction Cycle in the TEKO Facility

2. W. Schüller:
   Operating Experience with the WAK Reprocessing Plant in the Federal Republic of Germany

3. K.H. Neeb:
   Decontamination in Light Water Reactors - Techniques and Experiences

4. D. Ertel:
   Analysis of N-Containing Compounds in PUREX Process Solutions

5. F. Baumgärtner, R. Henkelmann:
   On the Necessity for Chemical Microdimensional Analysis of Radioactive By-Products in the Nuclear Fuel Cycle

6. G. Marx, A. Bestanpouri, W. Erben, D. Wegen:
   Radiochemical Investigations on Corrosion of Valve Metals

7. E. Henrich, U. Bauder, R. Marquart, W.G. Druckenbrodt, K. Wittmann:
   A New Concept for Product Refining in the PUREX Process

Neue Entwicklungen auf dem Gebiet der Wiederaufarbeitung

Unter diesem aktuellen Thema fand ein Seminar vom 3.-10. März 1984 in Obertraun/Österreich statt. Veranstalter waren die Gesellschaft Deutscher Chemiker (Fachgruppe Nuklearchemie), der Verein Österreichischer Chemiker, und das Institut für Heiße Chemie des Kernforschungszentrums Karlsruhe, das auch die Organisation übernommen hatte.

Aus nahezu allen Bereichen der Chemie und Verfahrenstechnik der Wiederaufarbeitung abgebrannter Kernbrennstoffe wurden insgesamt 28 Vorträge gehalten. Diese umfaßten Betriebserfahrungen an verschiedenen Versuchsanlagen und der Wiederaufarbeitungsanlage Karlsruhe (WAK), Fortschritte bei der Aufklärung des chemischen Mechanismus der Solvent-Extraktion, des Hauptverfahrensschrittes beim PUREX-Prozeß und deren Modellierung, neuere Entwicklungen in der Analytik und Prozeßkontrolle, spezielle Material- und Korrosionsfragen, sowie Beiträge zur Wartung und Instandhaltung von technischen Anlagen. Einen relativ breiten Raum nahm die Behandlung neuer Verfahrenskonzepte zur Vereinfachung und "Verkürzung" des PUREX-Verfahrens ein, deren technische Realisierung erst mittelfristig zu erwarten ist.

Es gelang nicht - wie bei früheren Seminaren dieser Art* - einen Tagungsband als Monographie herauszugeben. Ein Teil der Vorträge erschien in verschiedenen Ausgaben der Zeitschrift "Atomkernenergie/Kerntechnik". Diese sind in Übereinstimmung mit dem Verlag in diesem KfK-Bericht zusammengefaßt.

Um den Kreis der Interessenten möglichst weit zu halten, wurden die Autoren gebeten, ihre Beiträge in englischer Sprache abzufassen. Die Überarbeitung der Manuskripte hat T.V. Healy, Abington, UK, dankenswerterweise übernommen.

* Chemie der Nuklearen Entsorgung, Teil I und II (F. Baumgärtner, Hrsg.), Verlag Karl Thiemig, München 1978;

Chemie der Nuklearen Entsorgung, Teil III (F. Baumgärtner, Hrsg.), Verlag Karl Thiemig, München 18980;

Nukleare Entsorgung, Band 2 (F. Baumgärtner, K. Ebert, E. Gelfort, K.H. Lieser, Hrsg.), Verlag Chemie, Weinheim 1983.

Karlsruhe, Dezember 1986

K. Ebert
R. v. Ammon

Artikel vom Winterseminar in Obertraun, Österreich, 4. bis 10. März 1984, veranstaltet vom Institut für Heiße Chemie, Kernforschungszentrum Karlsruhe, in Zusammenarbeit mit der Gesellschaft Deutscher Chemiker und der Gesellschaft Österreichischer Chemiker

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Operating experience with the Karlsruhe reprocessing plant[1]

*By Walter Schüller**

Abstract

The Wiederaufarbeitungsanlage Karlsruhe (WAK) pilot plant, commissioned in 1971, has the longest operating record of all light-water reactor reprocessing plants. It provides a solid basis of experience for the planning and operation of the first industrial reprocessing plant in the Federal Republic of Germany. The paper gives a summary of 19 reprocessing campaigns and of 9 intervention programs devoted to plant maintenance, process improvements, and equipment development. It also summarizes our experience with process control equipment and sampling devices. In addition to routine process control and safeguarding fissile material inventory, the analytical staff services highly versatile facilities for evaluation of design data for the industrial plant. The safety record of the plant is outstanding.

Zusammenfassung

Betriebserfahrungen mit der Wiederaufarbeitungsanlage Karlsruhe

Die Versuchsanlage WAK hat seit ihrer Inbetriebnahme 1971 weltweit die längste Betriebszeit aller Wiederaufarbeitungsanlagen für Leichtwasserreaktor-Brennstoff erreicht und bildet eine solide Erfahrungsbasis für die Errichtung und den Betrieb der geplanten ersten deutschen industriellen Wiederaufarbeitungsanlage. In diesem Beitrag wird zusammenfassend über die bisher durchgeführten 19 Wiederaufarbeitungskampagnen berichtet sowie über 9 Interventionsprogramme, die sowohl Instandhaltungsarbeiten als auch die Einführung verbesserter Verfahren und weiterentwickelter Apparate umfaßten. Erfahrungen mit der Betriebsmeßtechnik und den Probenahmesystemen werden ebenfalls zusammengefaßt. Neben der routinemäßigen Analytik zur Prozeßkontrolle und zur Spaltstoffüberwachung bietet das analytische Laboratorium eine flexible Sonderanalytik, um im Rahmen von gezielten Untersuchungen Auslegungsdaten für die industrielle Anlage zu ermitteln. Die Bilanz des Strahlenschutzes der WAK ist in hohem Maß befriedigend.

DESCRIPTORS

WAK
OPERATION
SAFETY
RADIATION PROTECTION
MAINTENANCE
SAFEGUARDS
PROCESS CONTROL
REPAIR
INSPECTION

1. Introduction

Contrary to widespread opinion in this country, reprocessing as the final step in the fuel cycle has been actively pursued in the Federal Republic of Germany since the early sixties. Following an initiative taken by the chemical industry, the Federal Government decided to support the project of a national pilot reprocessing plant (Wiederaufarbeitungsanlage Karlsruhe, WAK) within the framework of the German Nuclear Energy Program.

The Karlsruhe Nuclear Research Center (KfK) was selected as the site of the plant; the capacity of 175 kg of uranium per day at a maximum of 200 operating days per year was in line with the expected fuel yield at the time of commissioning and was based on the light-water and heavy-water reactor fuels of the German nuclear power plant types of that time. Planning was carried out by the engineering consortium Uhde/Leybold/Lurgi in the early sixties, the applications for the construction permit were filed in August 1965 and, after the first construction permit had been granted, construction was started in January 1967.

At that time a licensing procedure of 17 months was regarded as complicated and lengthy; the overall time for construction and commissioning, which took 55 months, was kept on schedule and the budget of DM 60 million was not even completely used up.

So much for a nostalgic review of the early days of nuclear plant construction. Table 1 presents a summary of the main data and design features of WAK.

On September 7, 1971, WAK was commissioned with a first batch of FR-2 fuel elements, which had already been stored in December 1969. With almost fourteen years on-line, the WAK plant has the longest operating record of all LWR reprocessing plants worldwide and constitutes a solid background of experience for planning and construction of the first industrial reprocessing plant WA-350 planned by Deutsche Gesellschaft für Wiederaufarbeitung von Kernbrennstoffen (DWK) for the site of Wackersdorf, Bavaria.

Table 1: WAK design characteristics

Process	Head-End	Chop-Leach
	U/Pu-Separation and Decontamination	PUREX – 2 Cycles Mixer Settlers
	Tail-End	Silicagel (U); Ion-Exchange (Pu)
Fuels	UO_2 in Zircaloy-Cladding	(LWR, HWR)
	Max. Enrichment	3.5 % U-235
	Max. Burnup	40 GWd/tU
	Final Products	UNH-Solution 450 g U/l Pu-Nitrate-Solution 250 g Pu/l
	Plant Throughput	175 kg U/d up to 15 GWd/tU 105 kg U/d at 40 GWd/tU
Time Schedule	Planning	from 1964
	Licensing	(17 Months) Aug. 65 – Jan. 67
	Construction/Commissioning	(55 Months) Jan. 67 – Aug. 71
	Hot Operation	from Sept. 1971
Cost	Scheduled	DM 60 Mio
	Actual	DM 59.7 Mio

2. Working programs

2.1. General

In line with WAK's function as a pilot plant, only about half of the available time is scheduled for reprocessing campaigns. The balance is used for inspection, maintenance and repair of equipment and for the implementation of technical improvements and innovations during intervention programs on the basis of detailed preplanning and after previous decontamination.

Fig. 1 gives an overall balance of the time utilization over the approximately 4500 days from the commissioning of the plant to the end of 1983. Roughly an equal share of available time was used for reprocessing campaigns (46 %) and for interventions (42 %). Approximately 9 % of operating time is spent on startup and shutdown operations between campaigns and fissile material inventories. Within intervention periods, a comparatively high 19 % is required for plant decontamination, since WAK has been designed for contact maintenance.

In order to increase the available production capacity in an industrial plant, both fractions must be reduced, on the one hand, by combining fuel element batches into reprocessing campaigns of sufficient length and, on the other hand, by a higher degree of remote maintenance.

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[1] Revised from a paper presented at the winter seminar on new developments in the field of reprocessing, Obertraun, Austria, March 4–10, 1984, organized by the Institut für Heiße Chemie, Kernforschungszentrum Karlsruhe, in collaboration with Gesellschaft Deutscher Chemiker and Gesellschaft Österreichischer Chemiker.

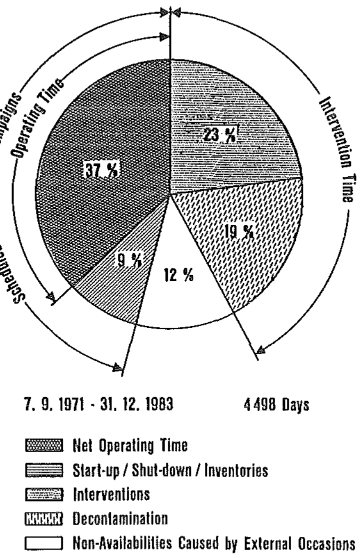

Fig. 1: Plant utilization 1971–1983

2.2. *Reprocessing campaigns*

Since the commissioning of WAK in September 1971, nineteen reprocessing campaigns of different lengths (26 to 241 days) have been carried out to reprocess fuel elements from five nuclear power plants (KWO, KRB, VAK, HDR, MZFR), one research reactor (FR-2) and one ship propulsion reactor (N. S. Otto Hahn) with a total content of 150 t of uranium and 720 kg of plutonium.

Fig. 2 is a diagram representing these reprocessing programs in terms of quantity, burnup and extracted energy of the fuel, for different reactor types. Particularly valuable experience has been accumulated in reprocessing LWR-fuels, representative of the WA-350 with average uranium burnups of about 30 GWd/t and cooling times between 2 and 12 years. This cooling time is another important factor because it determines the Zr-95 and Ru-106 content and the appropriate decontamination factors. For this reason, processing of heavy-water reactor fuels with short cooling times adds an important element of operating experience.

Three factors must be taken into account when determining the availability of the plant:

- As a pilot facility, WAK is on-stream for reprocessing only part of the time. Only this time plus the maintenance fractions of the intervention programs can be used as a basis for availability assessments.
- The plant was designed without any operational redundancy.

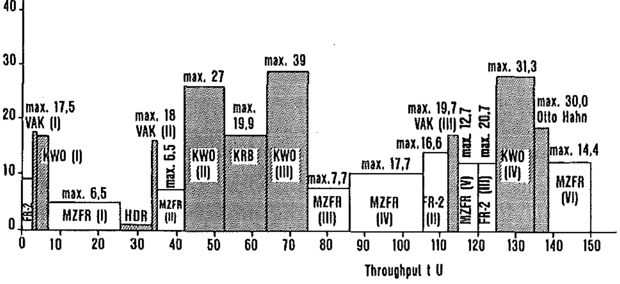

Fig. 2: Fuels processed in WAK

- The design uranium burnup of 20 GWd/t limits the Pu/U throughput ratio. As a consequence, reprocessing of fuel with higher burnup (and higher Pu content) decreases design throughput from 175 kg to 105 kg of uranium per day (at 40 GWd/t).

Fig. 3 shows this situation together with a compilation of the effective daily throughputs achieved for major reprocessing campaigns. It can be seen that these data follow the trend of the theoretical curve; plant availabilities range from 48 % to 84 % with an average of 67 %.

The Purex process, which has been well proven in all reprocessing plants since 1954, has also demonstrated its excellent performance in reprocessing LWR fuel elements with higher burnups. Typical decontamination factors for such fuels are between 2.2×10^4 (Zr) and 6×10^8 (Cs) for uranium and between 1.4×10^5 (Zr) and 2.7×10^8 (Cs) for plutonium. The partitioning factor of uranium and plutonium attains 5×10^3, ensuring that the specification of less than 10 ppb Pu in the uranium product is met after a subsequent purification step. Uranium and plutonium input analyses agree with burnup calculations within 0.1 % and 0.4 %, respectively. Fissile material losses in the waste add up to a total of 1.7% for uranium and 2.6% for plutonium. The residual enrichment of recovered uranium is between 0.15 % and 0.4 % U-235 for heavy water reactors, 0,7 % and 1.1 % for typical LWRs and up to 3 % for special fuels, such as that of N. S. Otto Hahn. Depending on residual enrichment, the U product is either precipitated as ammonium diuranate and stored or converted into UF_6 for re-enrichment.

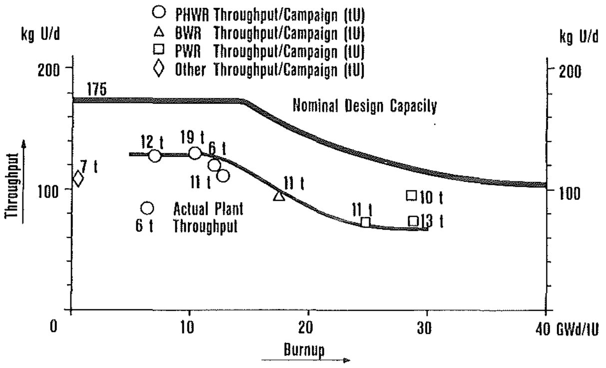

Fig. 3: WAK design capacity and actual plant throughput

A quantity of 54 m^3 of concentrated high-level fission product solution has been accumulated from reprocessing 150 t of uranium with a thermal energy equivalent of 2100 GWd. For the time being, this solution is stored in cooled high-level waste tanks at WAK prior to vitrification and eventual removal to the national repository. Low – and medium – level wastes are processed into waste packages by the Central Decontamination Service Department (HDB) of KfK, meeting the acceptance criteria of deep geological disposal. Table 2 is a summary of some data derived from practical experience, such as the volumes of the different waste categories, their volume reduction factors by conditioning, and technical data of the waste packages.

2.3. *Intervention programs*

With regard to the pilot plant function of WAK, reprocessing campaigns and intervention programs must be given equal importance. Since the commissioning date of the plant, eight different intervention programs have been

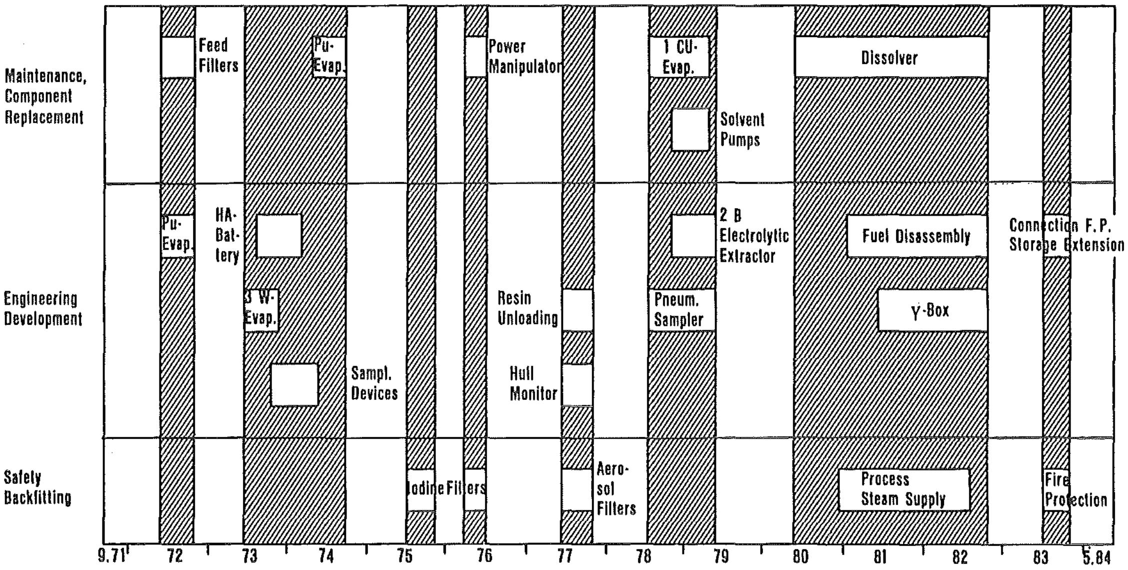

Fig. 4: Intervention programs in WAK

carried out, which are normally composed of numerous detailed projects and which require thorough planning and preparation. In a few cases, however, this preplanning was limited, because the initiating events were not known in advance. Fig. 4 shows a schematic diagram of the intervention programs, including the time sequence and major activities.

The reasons for each of the specific projects can be classified under three headings:

- maintenance and/or replacement of components,
- engineering development projects and in-plant testing of new or improved equipment,
- safety-backfitting of technical systems required by the authorities.

Although the principal activities may differ from case to case, intervention programs normally combine projects from each category and are performed in conjunction with the annual revisions of the utility systems. This makes it rather difficult to identify plant shutdown times caused by operational reasons.

The main activities of the past intervention programs consisted in installation of

- an improved HA extractor and a new Pu evaporator (1973/74),
- high-efficiency iodine filters (1975),
- an electrolytic extractor in the 2nd Pu cycle and pneumatic samplers (1978/79)

and replacement of

- the 1 CU intercycle evaporator (1978/79),
- the dissolver plus off-gas system and the fuel-element disassembling equipment (1980/82).

These new and improved systems added important contributions to operation experience, plant safety, improved health physics, environmental protection, and to increased plant availability.

The WAK plant was designed for contact maintenance, except for fuel disassembling, chopping and dissolver feeding operations, which are installed in a remotely operated hot cell and therefore offer a certain degree of remote maintenance capability. Most parts of the plant, however, require time-consuming decontamination prior to access of personnel. Process cells are rather densely packed with equipment and piping and present difficult working conditions, particularly if protective clothing is required. As in nuclear power plants, the work-load during intervention periods exceeds the capacity of our own staff, which must therefore be backed-up by contractor personnel.

Table 3 gives an impression of the time requirement and waste volumes for decontamination and scrapping of the installations in our mechanical head-end cell (size approximately 12 m × 6 m × 7 m) in preparation for dissolver replacement.

Starting with the normal operating radiation level of some

Table 2: Reprocessing waste categories
Uranium burnup 20...39 GWd/t

Waste Category	Activity	Primary Waste Amount m^3/tU	Conc. Factor	Package Volume m^3/Package	Solidification Matrix	Secondary Waste Volume m^3/tU	Secondary Waste Package No./tU	Activity Ci/Package
F.P. Concentrates (HAW)	high	0,6 - 0,8	~ 8	60	Glass	0,09	1,5	200000
Hulls and Structural Material	medium	1,6	1	200	Cement	1,6	8	10000
MAW-Concentrates		13 - 16	~ 5	200	Cement	2,6 - 3,2	13 - 16	~ 25
Resin Fixation		~ 0,05	~ 0,2	200	Cement	~ 0,25	~ 1	
LAW-Concentrates	low	80 - 100	~ 40	200	Cement	2,0 - 2,5	10 - 13	
LAW-Ashes		9	~ 50	200	Cement	0,18	~ 1	1

Table 3: Head-end cell decontamination

Procedure	Time required Months	Radioactive Wastes liquid MAW m^3	Radioactive Wastes Solid MAW m^3	Radioactive Wastes Solid LAW m^3	Radiation Level R/h
Internal Decont. of Process Equipment	4*	63	-	-	500
Remote Scrapping	10	-	86	-	10
Remote Decontamination	2	38	-	-	0,4
Direct Decontamination	3,5	80	10	17	0,03

* Included in "Remote Scrapping"

10^2 Gy/h, this dose rate was successively reduced to about 0.1 Gy/h by remote scrapping and removal of equipment, and further down to 0.3 mGy/h after remote pre-decontamination and final contact decontamination. This was considered an acceptable basis for the subsequent remounting of the new head-end facilities.

The WAK experience acquired during this dissolver exchange intervention has been analysed in detail, regarding overall workload, necessary decontamination effort, occupational exposure, waste yield, and cost figures. This analysis has supported and stimulated the decision of our shareholder DWK to provide a modular equipment-rack design (FEMO) and remote maintenance facilities for the high and medium active as well as the plutonium-bearing sections of the industrial plant WA-350.

3. Process control and safeguarding of fissile material

In addition to supervising plant operations, the WAK process control system provides all data for nuclear materials accountancy for the safeguarding of fissile material. The process control system is based on instrumentation and on analyses of process samples taken by remotely operated sampling devices.

Important devices of process control instrumentation include purged dip-tube systems for level and density measurement of process solutions, flow meters, and thermocouples. In addition, a number of special methods are used, such as ultrasonic detection of liquid-liquid interfaces in mixer-settlers and neutron counters for in-line monitoring of plutonium concentrations. In general, process control instrumentation applied in WAK has given satisfactory results. Occasional plugging of dip-tubes was caused by crystallization of uranyl nitrate, especially in evaporators. Orifice flow meters never gave rise to any disturbances. However, rotameters and rotary piston meters used in the chemical make-up facility have proved to be less reliable and are gradually being replaced by mass flow meters based on the gyrostatic principle. Thermocouples may be used in a reprocessing plant without any problems.

Due to the preventive maintenance of process control equipment, unexpected plant shutdowns due to failures of these devices have been avoided. Important features of process control instrumentation have remained unchanged since WAK start-up and therefore represent the technology of the late sixties. As a result of the extremely rapid development in that area, the design of the industrial plant will not use this type of instrumentation, but will incorporate up-to-date process control techniques. However, operational experiences of WAK will be considered in special cases.

The sampling facilities of WAK are the connecting link between chemical process and analytical control. They supply representative samples with high availability. Two different systems are applied by WAK, one of which delivers samples from 17 outlets of the extractors, whereas the other system is used for the sampling of 84 vessels. Each of these vessels is connected to one of 14 automatic sampling stations by suction and discharge pipes.

The process solutions are transferred by vacuum supported air-lift to the sampling station and recirculated through a 2-cm^3 sample bottle. The filled bottle is conveyed to the analytical laboratory by a pneumatic system.

Since start-up of the plant, some 260000 samples of radioactive solutions have been taken, approximately 40000 of which were taken by system I, and 220000 by system II. The failure rate of system I was about 0.5%, the failure rate of system II initially reached 1.5%, but could be reduced to as low as 0.2% by improvements on the steering mechanism. In the case of a failure, the average down-time for repair of a sampling facility is less than one hour. The sampling techniques developed at WAK have an excellent operating record in comparison with those applied at other reprocessing plants.

The analytical laboratory comprises a shift crew for routine analysis and special sections for Pu-analysis, spectrometry, quality control and tracer analysis. Ever since WAK has been in operation, the analytical facilities have been improved continuously and adapted to new techniques. Analytical requirements in reprocessing cover an extreme range of radiation levels and concentrations, which are met by a variety of methods. In order to determine plutonium concentrations, e. g., 14 orders of magnitude have to be covered, for which 8 different methods are applied. All 60 methods used are contained in an analytical handbook.

Apart from routine process control, WAK analytical staff contribute data to the design basis of the WA-350 by means of special investigations, as well as supplying the major part of the data used for fissile material safeguards at WAK.

The latter is based on material accountancy in accordance with the Euratom treaty and, since 1978, also on additional IAEA inspections, according to the verification agreement of the Nonproliferation Treaty.

During reprocessing campaigns, inspectors from both organizations co-operate as a joint team in controlling the fissile material throughput. During shut-down phases, safeguarding – in agreement with WAK – is achieved by placement of seals at strategic points.

For the purpose of fissile material accounting, WAK is divided into three material balance areas, in which every input and output is registered. In addition, the material inventory of each area is verified by physical inventory twice a year in the presence of inspectors. To date, neither plant operation in general nor the verification of fissile material accounting have given the inspecting authorities reason to request extraordinary inventories.

The division in charge of fissile material accounting and the technical divisions of WAK jointly participate in internationally coordinated research and development programs to improve the safeguarding of nuclear fuel.

4. Industrial safety and radiation protection

According to the high-ranking position of nuclear safety in the Federal Republic, our company pays particular attention to the areas of occupational safety and control of radioactive effluents.

At present, WAK employs a staff of 430, supplemented on certain occasions by up to 100 workers from outside contractors. Out of this grand-total, about 380 regularly work in the controlled area of the plant and have accumulated approximately 6.2 million hours of work since the WAK was commissioned.

This fact provides us with a representative statistical basis for our outstanding occupational safety record, which disproves the general opinion that work in a fuel reprocessing plant is extremely hazardous.

As far as the conventional accident-rate is concerned, a reprocessing plant may be compared with a chemical plant. Analysing the WAK accident-rate per 1000 man-years, we do not only observe a continuously decreasing trend, but register an average of 45 % of the corresponding accident-rates in the chemical industry. Only 74 % of the accidents are true occupational accidents; 26 % are caused by sports activities and occupational traffic. It is easy to prove that, in relation to the time involved in these activities, the largest occupational hazard in reprocessing is that of driving to work by car every day.

The safety record in radiation protection is equally impressive. Fig. 5 shows the annual number of body contaminations and incorporations of radioactive material in relation to the total number of supervised staff. Apart from the continuous decrease of these events, we note a relation of staff to annual contaminations and incorporations of roughly 100 : 10 : 1 and an absence of any cases of incorporation since 1979.

Occupational doses by external radiation in the WAK plant were reported on several occasions. Compared to the maximum permissible occupational dose of 50 mSv/a (5 rem/a), the average dose of WAK personnel decreased from an initial 30 % to a standard of 4 to 8 % since 1975 – a result of increasing experience and a rigorous policy of dose minimisation. Individual doses – with a single exception – never reached or exceeded the legal limits.

This outstanding record has not been achieved by distributing the doses among an increasing number of personnel, which is reflected in the collective dose encountered in operation of the WAK plant. Fig. 6 shows a radiological operating diagram of collective dose versus reprocessed energy-equivalent for 13 years of WAK operation together with figures from the Eurochemic plant. Except for the trial phase of initial operation, these data can favorably compare even with those of production plants like La Hague, although the staff-to-throughput ratio in a pilot plant is much higher and therefore less favorable to this type of statistics.

Fig. 7 gives a summary of 112 so-called safety-related events from 1971 to 1982 and their breakdown into plant sections. The most remarkable observation is the fact that the majority of such events occur in the general utilities and auxiliary process sections.

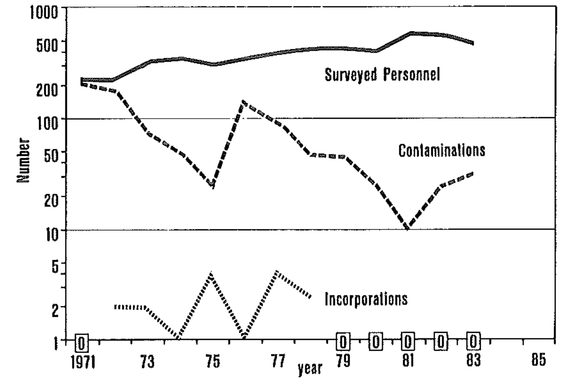

Fig. 5: Contaminations and incorporations

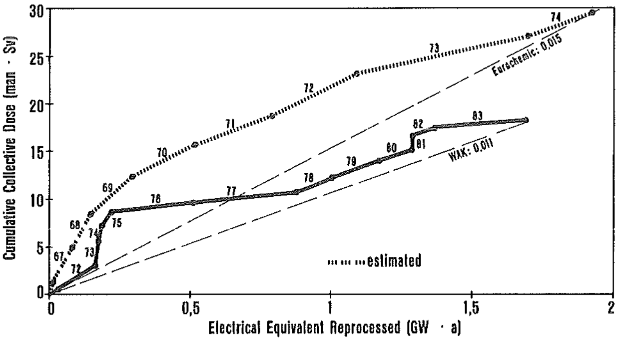

Fig. 6: Occupational radiation exposure in reprocessing plants

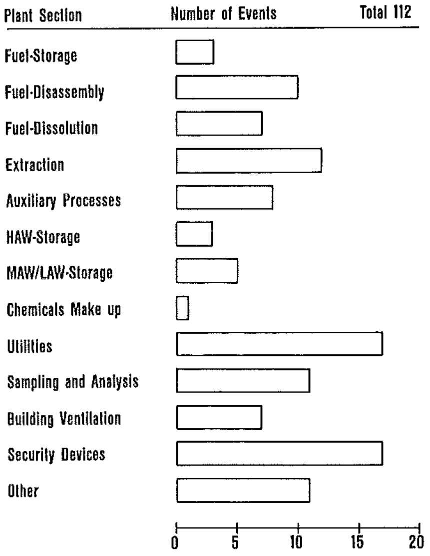

Fig. 7: Safety related events in WAK 1971–1982

5. Emission control

The maximum possible retention of radioactive releases and continuous monitoring of the remaining emissions with gaseous and liquid effluents are major contributions to the protection of the environment of nuclear facilities.

Liquid effluents from the WAK plant are pretreated by the KfK Central Decontamination Department and discharged into the Rhine river together with effluents from other facilities on site.

Gaseous and aerosol releases from the WAK stack are part of an overall emission plan for the KfK, which must be licensed every year. For WAK, the gaseous releases of I-129, I-131, Kr-85 and, to a lower extent, C-14 and H-3 must be taken into account. For aerosols, a distinction is made between α- and β-aerosols; among the latter, Sr-90 is monitored separately.

It is not possible, within the scope of this paper, to go into the details of retention techniques for airborne radioactivity, the methods employed for continuous monitoring of stack releases, and the extensive radioecological survey programs, carried out by the KfK and independent environmental protection authorities. In the course of 13 years of operation, not only the number of nuclides to be monitored have been increased, but the discharge levels have successively been reduced by substantial factors. Nevertheless, WAK has been able not only to meet, but to stay considerably below the increasingly restrictive requirements, e. g., by employing newly developed retention methods for radio-iodine.

On the basis of today's retention techniques, demonstrated in actual operation, the WAK plant can limit its emissions to levels between 4 % and 20 % of those fixed in the emission plan.

The current practice of calculating the environmental impact of radionuclides on the basis of monitored stack releases is extremely conservative, which was demonstrated in a radiological survey comparing calculated immissions of iodine in the neighborhood of WAK with real in-situ measurmenents in goat milk and specimens of game. Although these samples were taken near the immission maximum over a period of two years, the results were lower by 2 orders of magnitude than the calculated data. We believe that further radioecological studies are required to demonstrate the large safety margin between theory and practice in this field.

By transferring the WAK emission data to the larger throughput, different site meteorology and stack height of an industrial plant, it can be proven that the WA-350 plant, given the most adverse conditions, will cause a calculated whole-body dose at the point of maximum impact in the order of 50 to 70 μSv/a (5 to 7 mrem/a).

6. Transfer of experience and training of personnel

WAK is operated to advance reprocessing techniques and to train personnel in planning, construction, and operation of a large-scale reprocessing plant. Feeding operating experience into the planning of the WA-350 plant is one of the key activities.

Since the first conceptual design in 1973, WAK has been continuously involved in the planning of a large industrial plant. Thus the operating experience of the pilot plant is utilized for industrial application. As the design of the WA-350 plant is now being consolidated, our contribution is concentrated on the training of operating personnel and on important developments, which promise a gain in operational safety and a cut-down of operational costs.

Staff training has been one of our major activities since the foundation of our company in 1964. Prior to the commissioning of WAK, staff members participated in the operation of the Eurochemic reprocessing plant in Mol, Belgium, and gained experience in production plants of the chemical industry. Nevertheless, the background of experience at the time of the WAK start-up was rather limited. Today we have a technical staff representing 3600 man-years of practical experience in reprocessing. During recent years we have increasingly been involved in the training of DWK personnel for the operation of the WA-350 plant. This will also be the main task in the near future.

Apart from introducing the personnel of the future plant to the technology and management of reprocessing, for almost 10 years WAK has fulfilled its duty to inform the public on plant operation and to show that this is done in full responsibility and awareness of safety regulations.

From 1976, a total of 20 500 visitors have been introduced to WAK, mostly from sites which were being considered for an industrial plant. By far the majority of these people reached, according to their own opinion, a positive attitude towards reprocessing. To ease acceptance by convincing is indispensable not only to make mature reprocessing technology available but also to use it on an industrial scale to close the nuclear fuel cycle.

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Uranium extraction cycle in the TEKO facility[1]

*By Klaus Eiben and Heiko Zimmermann**

Abstract

Construction and operation of a complete extraction cycle for simulation of the Purex process with depleted uranium at the TEKO facility (Teststand für Großkomponenten, testing facility for full-scale components) has provided valuable information for the design of extraction equipment for a commercial reprocessing plant. This applies particularly to pulsed HA and C columns where typical hydrodynamic phenomena and problems, in addition to scale-up tasks, had to be solved. The working behaviour of the individual apparatus and of the entire equipment has been tested in detail. Simulation of typical malfunctions of the plant have been carried out. New ways of processing (electrolytic reoxidation, removing tributyl phosphate from aqueous raffinates by steam stripping, direct and careful distillation of the organic solvent, use of a mechanical pulsator in the pulsed columns) have been assessed under plant conditions.

Zusammenfassung

Uranextraktionszyklus in der Anlage TEKO

Der Bau und Betrieb einer kompletten Extraktionsanlage in der Anlage TEKO (Teststand für Großkomponenten) für die Simulation des Purex-Prozesses mit abgereichertem Uran hat für die Auslegung von Extraktionsapparaten für eine industrielle Wiederaufarbeitungsanlage wertvolle Erkenntnisse gebracht. Dieses gilt insbesondere für die Pulskolonnen C und HA, bei denen neben der Maßstabsvergrößerung typische strömungsdynamische Phänomene und Probleme beim Benetzungsverhalten zu lösen waren. Das Betriebsverhalten einzelner Apparate und der Gesamtanlage konnte im Detail untersucht werden. Simulationen von typischen Betriebsstörungen werden durchgeführt. Neuartige Verfahren (elektrolytische Reoxidation, Abtrennung von Tributylphosphat aus wäßrigen Raffinaten mit Wasserdampfdestillation, direkte und schonende Destillation des Extraktionsmittels, Einsatz eines mechanischen Pulsators für die Pulskolonnen) werden unter betriebsmäßigen Bedingungen erprobt.

DESCRIPTORS

PUREX PROCESS
SIMULATION
MOCKUP
CONSTRUCTION
DESIGN
OPERATION
PERFORMANCE TESTING
SOLVENT EXTRACTION
EXTRACTION COLUMNS
TBP
REMOVAL
DISTILLATION
FUEL REPROCESSING PLANTS
DEPLETED URANIUM

1. Introduction

The uranium extraction cycle facility is used for equipment testing and to assess possible processes for the first extraction cycle of a commercial reprocessing plant with a daily capacity of 4 tons of heavy metal. This full scale (1:1) plant is one of the test facilities for large-size components operated for the Deutsche Gesellschaft für Wiederaufarbeitung von Kernbrennstoffen by the Research Department of the Wiederaufarbeitungsanlage Karlsruhe Betriebsgesellschaft mbH (WAK) [1].

This uranium extraction plant was built in the TEKO (Teststand für Großkomponenten, testing facility for full-scale components), a 1000 m^2 testing area within the Nuclear Research Centre at Karlsruhe. The contractors, an engineering group of Uhde GmbH /Kraftanlagen Heidelberg, put the plant into operation in autumn 1981. Since the summer of 1982 the plant has been operated with depleted uranium.

The uranium extraction cycle facility consists of five extraction columns, one mixer-settler for tritium stripping, two mixer-settlers for washing the raffinates, one prototype mixer-settler for the uranium clean-up cycles, and two mixer-settlers for washing the solvents, plus accessory facilities (Fig. 1). Using this simulated Purex process, uranium is extracted in the first column (HA) by 30 % tributylphosphate (TBP) in dodecane from the aqueous acid feed solution (2 to 3 M HNO_3) mixed with typical, inactive fission products. The organic (TBP) phase is washed by counterflow in the second extraction column (HS 1) and then separated in a multi-stage mixer-settler (HS 2) from entrained tritium. This tritiated water is simulated in the uranium extraction cycle using D_2O or short-lived radioactive tracers. In the third extraction column (1 BX) where uranium/plutonium separation normally takes place, uranium IV solution is fed in by metered addition as a reducing agent, and the hydraulic behaviour of its distribution is examined. In this uranium extraction facility no plutonium solutions are used.

In the fourth extraction column (1 BS), uranium is extracted into the organic phase from the aqueous solution, which in a non-simulated Purex system would contain the plutonium. In the last extraction column (1 C), refined uranium is finally re-extracted at a higher temperature (60° C) from the organic phase by means of dilute acid (< 0.1 mel/l). As an alternative, re-extraction can also take place in a twelve-stage mixer-settler designed for a throughput of 8 tons of uranium per day. Three evaporators contribute to recycling of the product flow in the uranium extraction plant: a natural circulating evaporator (2.5 m^3/h) is used for the upgrading of aqueous uranium solutions (1 CU); for the regeneration of nitric acid a vacuum evaporator with downstream rectification (0.8 m^3/h) is employed. The latter supplies a concentrated nitric acid (11 M solution) and a distillate, which, as in the uranium evaporator system, is fed back into the process. Before the solutions reach the evaporators, dissolved and entrained organic solvent (30 % TBP/dodecane) is washed out by dodecane in multi-stage mixer-settlers. The dodecane wash from the raffinate scrubbers is also recycled. A thin-film vacuum evaporator (0.15 m^3/h) is available for this operation. As an alternative to the extractive separation of TBP, a separation process using water vapour (TBP stripper) can be studied in a separate facility.

The organic solvent (2.3 m^3/h) is freed of hydrolytic products by alkaline and acid washes and is recycled. The stripping solutions from the scrub process are discharged as liquid waste (LAW).

Solution transfer in the extraction system is effected by airlift as in a reprocessing plant. Measurement and control of process flow is adjusted to the required process operating conditions. For the preparation of acids, a continuous process is used with static mixers via dosage and control systems and also in-line measurements. Two intermittently operating electrolytic cells are available for the production of uranium IV solutions. Hydrazine is used for the stabilization of U-IV solutions, and the excess is destroyed by means of an electrolytic cell (ROXI).

By the end of 1984, 360 t of depleted uranium had been

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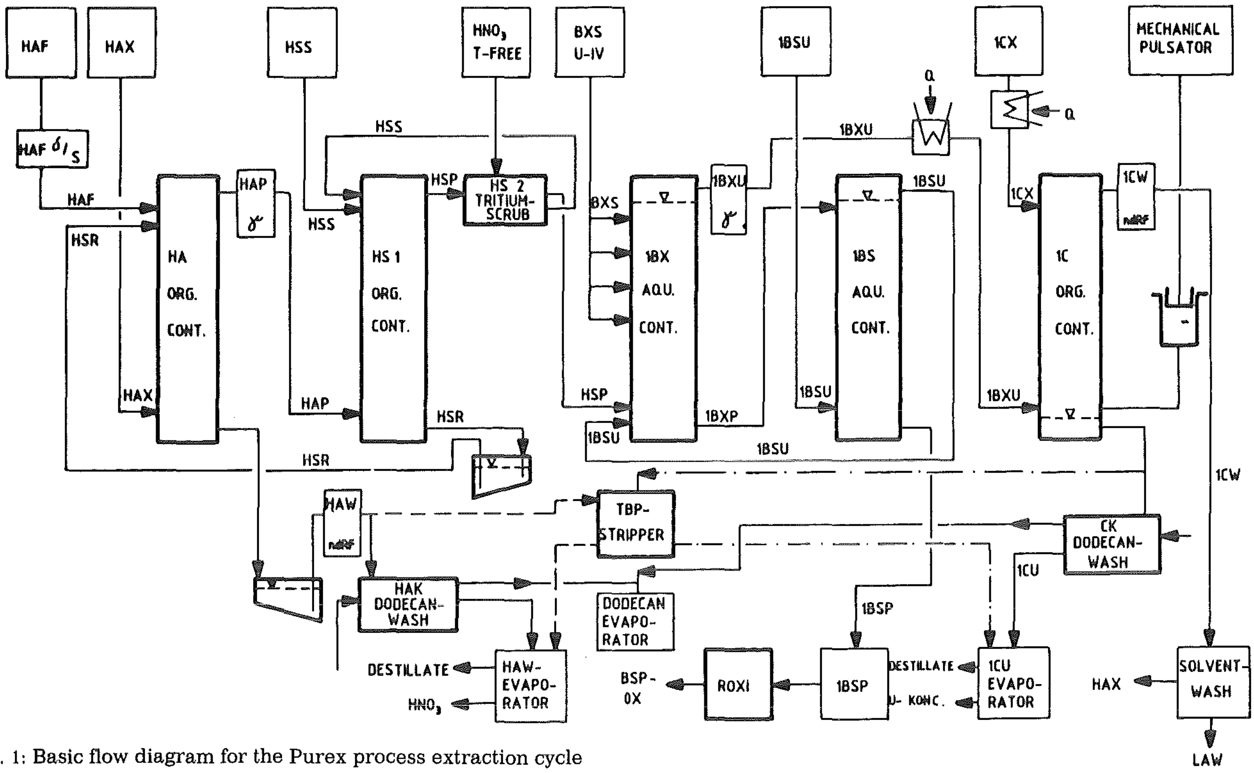

Fig. 1: Basic flow diagram for the Purex process extraction cycle

recycled in the facility, partly in shifts lasting several weeks. Single and compound operations have been tested in all parts of the plant, including both the 5 column process and all accessory operations. During this period, the 9 t uranium inventory was recycled 40 times.

In the following section we report on the experience gained in this work, which was particularly helpful during the scale-up and lay-out of the apparatus and the procedures to be used. This work will also help in minimizing planning risks during the construction stage of a commercial plant.

2. Extraction columns

Fluid-dynamic tests with the extraction columns have confirmed the construction data relating to throughput and mass transfer with the result that parameters of the industrial equipment (length, diameter, settling times) can be derived from the results obtained in the uranium extraction cycle. The load range of the individual extraction columns has been determined as a function of pulse frequency and pulse amplitude. The working points (operational mode) are within a range of 50 to 60 % below the flooding point and make allowance for the fact that there exists an adequate reserve for any decrease of the load range during the service life of the apparatus. Mass transfer tests were carried out above all with the HA and C pulsed columns.

As regards the C column, it was found that the organic dispersive operating mode – as originally provided – could be maintained for short periods only. This was because increased wetting of the organic phase at the sieve plates caused column flooding. This phenomenon sometimes occurred after only a few operating hours and considerably impaired the availability of back-extraction. When this happened, the situation could only be restored to normal by time-consuming rinsing and cleaning operations. Because of this, the column operation was changed over to the aqueous dispersive mode. The interface is now located in the bottom decanter of the column. The flooding point of the column has since then remained unchanged, and extraction efficiency has been satisfactory ever since. Fig. 2 shows typical column profiles for a throughput of 2.15 m³/h, an organic to aqueous phase ratio of 1 : 1 and for different pulse parameters. Back-extraction of uranium from the organic phase is obtained under any operating conditions up to 5 mg/1.

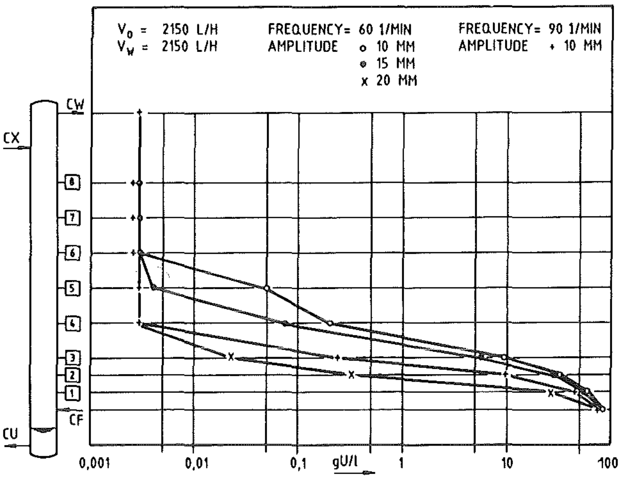

Fig. 2: Measurement of the C column profile (U, organic phase)

Up to the present, the aqueous dispersed operating mode offers advantages over the organic dispersed mode in the C column, both in processing and in operational technology. Experiments with mechanical pulsators have also been carried out in the C column since the end of 1983. Mechanical pulsation is an alternative to the originally conceived air pulsation in the extraction columns. In the upper lateral pulsation pipe, a hydraulically driven piston plunges into the operating liquid – in most cases the organic phase – of the extraction column. As a result of the upward and downward strokes, pulsation is transferred to the contents of the column. TBP serves as the hydraulic medium for the drive of the piston. With the mechanically driven pulsator the pulse parameters can be varied within a range that cannot be reached by air pulsation. Frequencies up to 2 Hz can be reached with sufficiently wide amplitudes. The object of the tests was to determine the optimal parameter ranges of frequency and amplitude. It had already been realized that with a constant pulsation intensity, relatively small amplitudes and high frequencies, a better separation performance is obtained than with relatively large amplitudes and low frequencies. From an economic point of view, however, mechanical pulsators offer savings of pulsation air of approx. 1000 kg/h for the pulsed columns in the first extraction cycle. Aspects of wear are studied in fatigue tests. The result of the tests will, in turn, be utilized in preparing a service and maintenance concept for the planned commercial reprocessing plant WA-350.

Mass transfer in the HA column was examined under varying operating conditions. This column is equipped with nozzle plates and is operated in the aqueous dispersed mode. Phase separation is effected in an external decanter. A report on the hydraulic behaviour has already been given [2].

During mass transfer measurements across the active length and the cross section of the HA column, unsatisfactory radial mixing behaviour has been observed. Irregular mass transfer was observed across a wide range of the active length of the column. As can be seen from Fig. 3, a fully satisfactory result can only be obtained at an amplitude of 25 mm and a frequency of 1 Hz. In the other cases, the full active length is needed for uranium separation up to 5 mg/l. The experience gained by profile measurements has been verified by radioactive tracer tests carried out by the Laboratorium für Isotopentechnik of the Karlsruhe Nuclear Research Centre [3].

To improve radial mixing, the distributor for the aqueous dispersed phase was altered. In addition, a number of specially designed distributing plates were installed to replace a corresponding number of nozzle plates. By this change, mass transfer was compressed to half the active length of the column but, as the distribution plates have reduced free cross section (14%), the load range of the column has been restricted. We are now looking for a compromise – redesigning the distributing trays – which optimizes mass transfer and provides a wider hydraulic load range. The working behaviour described here results from the coincidence of various effects of the extraction process. The organic continuous operating mode is actually preset, because the separation layer and the interfacial cruds likely to be met with should not be located close to the production outlet. The product is discharged at the head of the column. Thus the separation layer is located at the outlet of the aqueous phase (HAW). The aqueous uranium containing feed solution is, on the other hand, highly concentrated and has, at the inlet, a density which is higher by 50% than that of the organic phase. The organic to aqueous phase ratio (2.5) must be regarded as another handicap. Obviously the phase with the smaller volume flow must be dispersed. This will result in a relatively low aqueous hold up, i. e., a reduced specific exchange area. The nozzle plates installed in the HA column for reasons of more favourable wetting behaviour prevent – at least in the upper section of the column – a new preferred drop formation. The installation of distributing plates has, in fact, improved the mixing process. The phenomena described here occur, in such a distinct way, only in large diameter columns [4], and have not been noticed in small diameter (100 mm) test columns.

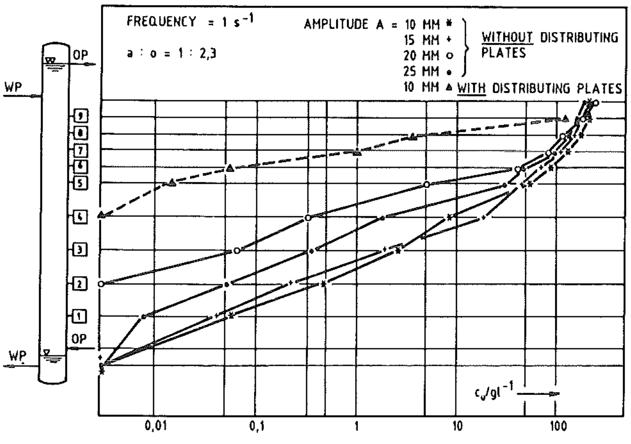

Fig. 3: Measurement of the HA column profile (U, aqueous phase)

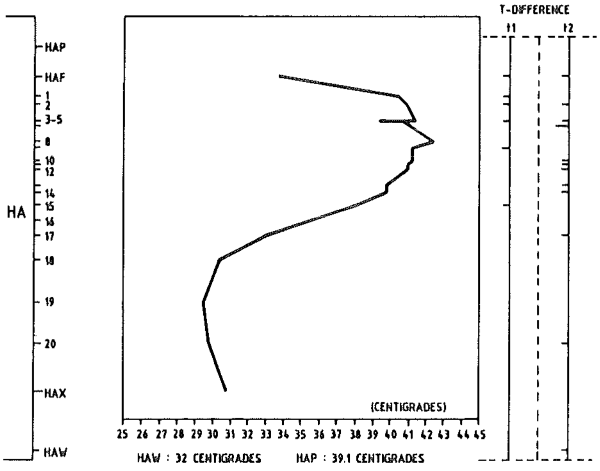

Fig. 4: Temperature profile in the HA column

During mass transfer from the aqueous to the organic phase, heat is released in the HA column. This can be measured as a temperature profile and utilized as helpful information during process control. A typical temperature profile is shown in Fig. 4.

The HA and HS 1 columns, operating in an aqueous disperse mode, are equipped with external decanters in which interfacial crud can be removed by suction without disturbing column operations. In each column, the aqueous phase, along with approx. 30% of the continuous organic phase, is taken from the lower end of the column and transferred via airlifts to the external decanter where it is separated into two phases. The organic phase is subsequently re-transferred to the column. The control systems and the airlift control for the withdrawal of the mixing phase have proved to be reliable. It is believed that by the proposed experiments, even with deposition in the boundary range, factory working behaviour will be demonstrated even under extreme operating conditions. A special design of a tubular decanter, which is geometrically safe as regards criticality, is also under test.

3. Mixer-settlers

The mixer-settlers, which were specially developed for extreme external phase ratios for washing the raffinates and for stripping tritiated water, have been hydraulically adjusted, for use for solutions both with and without

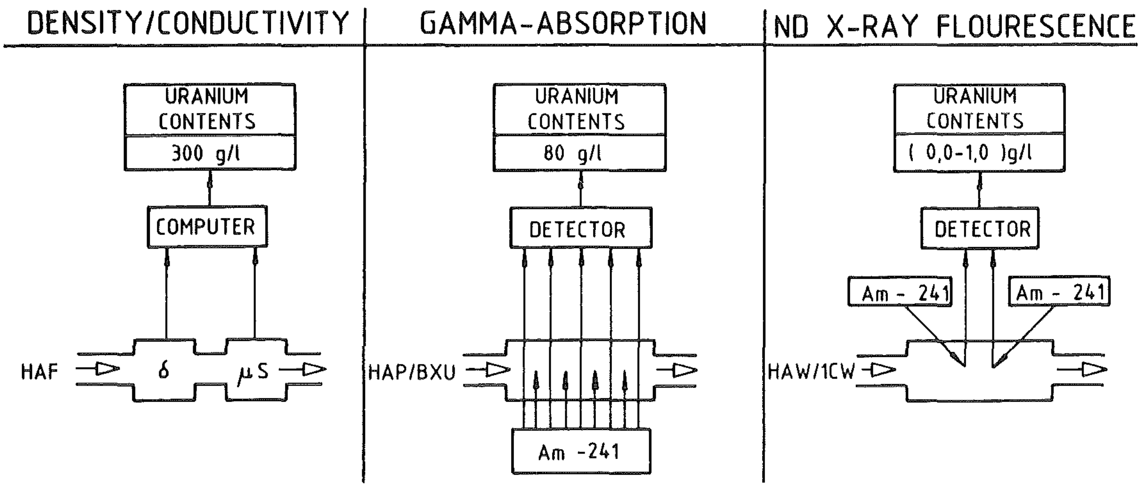

Fig. 5: Outline sketch of in-line instrumentation in the plant

uranium [5]. Mass transfer has been tested for the three-stage HAK and CK mixer-settlers for raffinate combined operations with the HA and C columns. TBP content in HAW and CU should, in both cases, amount to 3 mg/l after the 3rd stage. With an initial concentration in HAW up to 500 mg/l of TBP – of which up to 300 mg/l may be regarded as dissolved, depending on the solubility, while the remainder may be regarded as entrained – this object is also attained with organic to aqueous phase ratios of up to 1 : 80. TBP was also stripped from CU in the three-stage, CK mixer-settler up to the detection limit (3 mg/l). The simulated failure of a mixer-settler, regarded as a typical malfunction if it occurs in the first or second chamber of the HAK or CK mixer settler, is governed by the loss of a stage.

A gravity mixer-settler typical for the uranium cycle has been tested for back-extraction. The apparatus reaches the expected back-extraction values, i. e., uranium is stripped in twelve stages from the organic phase at 60°C up to 5 mg/l. Operational experience has shown that design changes can also contribute to increasing both the operational reliability and the working efficiency. Thus it was observed that the operating mode must be kept in the stable aqueous continuous phase in order to ensure short phase times. Using this apparatus the effects of simple malfunctions or of the failure of temperature controls on the operating results have also been assessed and evaluated.

4. Service facilities

The operation of service facilities has given valuable experience. This particularly applies to the in-line instruments as outlined in the basic flow chart (Fig. 1). Density/conductivity has been used as measuring principle in HAF, gamma absorption for HAP and BXU and non-dispersive X-ray fluorescence for high-level radioactive waste (HAW) and organic CW (Fig. 5). The density/conductivity measurement with an accuracy of ±1.5% and an acid concentration of 3 mol/l and a uranium concentration of 300 g/l has proved to be reliable for the preparation and control of feed solutions.

Gamma-absorption with a measuring accuracy of ±5% in the range of 80 g uranium per litre has served as valuable information for process control. Concentration variations in the HAP and BXU have been recognized at an early stage.

The non-dispersive X-ray fluorescence is used as a threshold measure to signal uranium breakthroughs of 50 mg/l in the HAW and CW. In the region of 50 mg/l as mentioned here, although the accuracy of measurement was only ±50%, it is nevertheless quite helpful in recognizing fast "uranium breakthroughs" from 10 mg/l upwards as demonstrated in simulated malfunctions. Operational experience gained with these instruments will be utilized in further research and development work which may lead to the application of in-line instruments in the cleaning cycles of a reprocessing plant. Their utilization in the first, high-active cycle calls for a higher degree of accuracy, in order to discriminate between disturbances caused by other dissolved metals (Zr, etc.) and by radiation.

Recycling of dodecane produced by raffinate washes has been successfully demonstrated. So far 120 m^3 of TBP-free dodecane have been recovered from organic waste. The concentrate (approx. 90% of TBP in dodecane), after dilution to 30% and after alkaline washing (scrubbing), has been recycled to a considerable extent. This caused no operational or instrumental problems. It is an advantage in the effective distillation that it is not necessary to use any extraneous chemicals. A careful distillation of the organic solvent from the uranium extraction cycle (25 m^3) was also exercised within the evaporator. In this process, accumulated decomposed products, which were not separated by alkaline or acid washing, were effectively separated here.

Acknowledgment

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Analysis of nitrogen-containing compounds in Purex solutions[1]

*By Dieter Ertel**

Abstract

The analytical assay of nitric acid, nitrous acid and hydrazine, and also of hydrazoic acid, hydroxylamine and ammonium in Purex process solutions is described and characterized using specific analytical methods, with typical concentrations quoted. The first three compounds, being familiar constituents in the Purex process, are analyzed on a routine basis using proven methods. Novel analytical approaches have been tested and introduced at the author's Institute to assay the other nitrogen compounds. Their application in the analysis of actual Purex process solutions gave interesting preliminary results, e.g., on the behaviour and concentrations of HN_3 and NH_4^+ found in the Purex process.

Zusammenfassung

Analyse stickstoffhaltiger Verbindungen in Purex-Prozeßlösungen

Die analytische Bestimmung von Salpetersäure, salpetriger Säure und Hydrazin sowie von Stickstoffwasserstoffsäure, Hydroxylamin und Ammonium in Purex-Prozeßlösungen wird beschrieben und anhand typischer Analysendaten charakterisiert. Die ersten drei Verbindungen werden als traditionelle Purex-Komponenten mittels bewährter Methoden routinemäßig analysiert. Dagegen sind für die letztgenannten Stickstoffverbindungen im Institut des Verfassers neue analytische Möglichkeiten erprobt und eingeführt worden. Ihre Anwendung zu analytischen Untersuchungen von realen Purex-Prozeßlösungen lieferte interessante vorläufige Ergebnisse, beispielsweise über das Verhalten und das Konzentrationsniveau von HN_3 und NH_4^+ im Purex-Prozeß.

DESCRIPTORS

PUREX PROCESS
NITROGEN COMPOUNDS
ORGANIC NITROGEN COMPOUNDS
NITRIC ACID
NITROUS ACID
HYDRAZINE
HYDRAZOIC ACID
HYDROXYLAMINE
AMMONIA
NITRITES
SOLVENT EXTRACTION
QUANTITATIVE CHEMICAL ANALYSIS
SENSITIVITY
PROCESS SOLUTIONS

1. Introduction

The Purex method for reprocessing spent nuclear fuels relies on the efficient separation of fissile materials and fission products through extraction with tributyl phosphate. It has proven its worth for decades and has now attained such a degree of technical maturity that alternative techniques have become unimportant [1].

The nitrogen compounds occurring in Purex process solutions are listed in Fig. 1 in the order of the formal oxidation number of nitrogen. The pK_a-values of the compounds are also indicated. It can be recognized immediately from their sizes which particular species occur in the (acid) process solutions. The "traditional" constituents are NO_3^-, HNO_2 and $[N_2H_5]^+$. Hydroxylamine as a potential reductant has a special place in the separation cycle and both hydrazoic acid and ammonium have attracted interest in recent years for a variety of reasons.

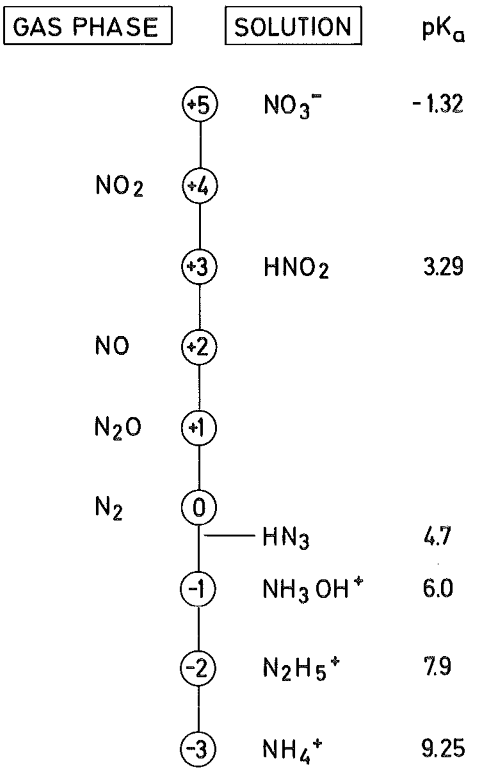

Fig. 1: Nitrogen species occuring in the Purex process

There are a number of possibilities for analyzing these nitrogen compounds. But in this article only those analytical methods are indicated which have proven their value in routine work of the Hot Chemistry Institute (IHCH) or have been specifically developed there within the framework of research and development studies.

2. Nitric acid

The nitrate content of process solutions is fixed by the sum of the dissolved salts of actinide and fission product elements and the so-called "free acid" (HNO_3). Normally, the nitrate content is not the subject of routine analysis, although in principle it can be recorded, e.g., by nitrate sensitive potentiometry [2]. In contrast, knowledge of the HNO_3 concentration is of fundamental importance because it exerts a strong influence on extraction behavior and hence on the control of the complete process.

The analytical assay of "free acid" in Purex process solutions has a long history which is characterized by a multitude of aspects [3]. In general, alkalimetric titrations are performed and the analytical problem consists in the elimination of U and Pu hydrolysis effects during neutralization. For complex formation we prefer a fluoride/oxalate mixture with a broad effect and use the electrochemi-

Table 1: Nitric acid determination

Automated potentiometric titration using 0.1 NaOH neutralization; U,Pu complexation by fluoride/oxalate mixture to suppress hydrolysis

Range	0.01...14 mol/l HNO_3 ($[HNO_3]/[Pu]$ >0.1)
Precision	0.5...3% relative standard deviation
Instrument	Radiometer Titrator TTT 60

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[1] Revised from a paper presented at the winter seminar on new developments in the field of reprocessing, Obertraun, Austria, March 4–10 1984, organized by the Institut für Heiße Chemie, Kernforschungszentrum Karlsruhe, in collaboration with Gesellschaft Deutscher Chemiker and Gesellschaft Österreichischer Chemiker.

cal potential of a glass electrode as the equivalence indicator (Table 1). This method is suitable for analyzing both aqueous and organic solutions; the latter are analyzed by stripping titration. High activity solutions can also easily be titrated in this way by remote operation [4].

In the presence of hydrazonium salts (e.g., in the separation cycle) care must be taken because their hydrolytic decomposition according to

$$[N_2H_5]^+ + H_2O \rightleftarrows N_2H_4 + H_3O^+, \; pK_a \; 7.9,$$

is not eliminated by the complexing process mentioned above with consequent free acid formation. However, the equilibrium constant of hydrazonium hydrolysis clearly differs from the neutral point, and therefore good automatic titrators yield two consecutive inflection points in the titration curve; this permits perfect separation of the two effects.

3. Nitrous acid

Due to radiolytic decomposition of NO_3^-, both aqueous and organic process solutions always contain small amounts of HNO_2. Sometimes NO_2^- and NO_2, respectively, are added intentionally, e. g., in order to destroy hydrazine or to adjust the valency of uranium/plutonium. Sensitive photometric HNO_2 analyses can be carried out by nitrous acid initiated diazotation of sulfanilic acid, followed by coupling with α-naphthylamine; this reaction produces a deep-red azo dye (Fig. 2) [2,5].

Given the specific nature of the color reaction and the color intensity, the analysis can normally be carried out using a high degree of dilution which practically eliminates potential influences of other reaction partners present in the solution.

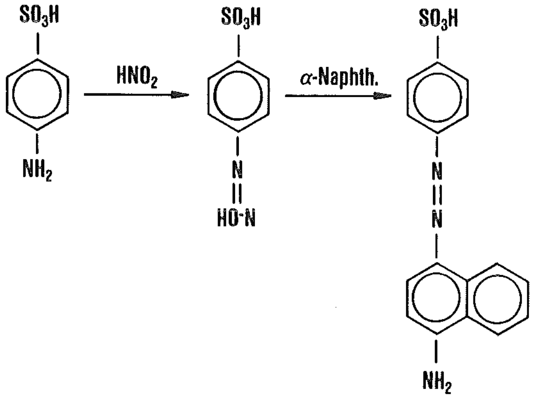

Fig. 2: Nitrous acid determination by spectrophotometry of azo dye from the Griess reaction. λ_{max} = 522 nm; ε_{max} = 4×10⁴ l/mol cm; range 2...30 µg NO_2 per 25 ml; limit of detection 20 ppb (5×10⁻⁷ mol/l); precision 1...3% relative standard deviation. Instrument: PMQ 3 (Zeiss)

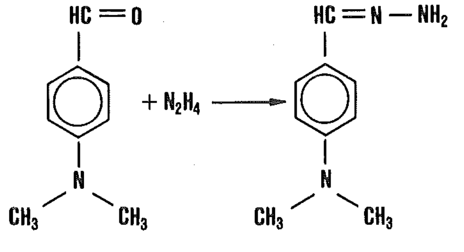

Fig. 3: Hydrazine determination by spectrophotometry of azomethine compound formed by reaction of hydrazine and p-dimethylaminobenzaldehyde. λ_{max} = 457 nm; ε_{max} = 6×10⁴ l/mol cm; range 0.2...5 µg N_2H_4 per 10 ml; limit of detection 10 ppb (2×10⁻⁷ mol/l); precision 1...3% relative standard deviation. Instrument PMQ 3 (Zeiss)

The HNO_2 content in organic solutions is transferred by Na_2CO_3 stripping into the aqueous phase where it is analyzed as above.

4. Hydrazine

In order to avoid autocatalytic oxidation reactions by HNO_2, hydrazine is added to the process solutions in the separation cycle. It acts as "nitrite scavenger" and in this way stabilizes the reductants U(IV) and hydroxylamine (HAN).

Hydrazine analysis is based on its reaction with p-dimethylaminobenzaldehyde [6,7], which produces a deep-yellow azomethine compound (Fig. 3). Photometric determination of its color intensity provides the basis for the specific and sensitive analytical method which is used to eliminate cross influences from other reaction partners present in the solution under condition of high dilution; within realistic limits hydroxylamine does not interfere with this type of hydrazine analysis.

5. Hydrazoic acid

In the purex process HN_3 is formed as an interim product of hydrazine oxidation by HNO_2 according to

$$\begin{aligned} [N_2H_5]^+ &+ HNO_2 \rightleftarrows HN_3 + 2\,H_2O + H^+, \\ HN_3 &+ HNO_2 \rightleftarrows N_2 + N_2O + H_2O. \end{aligned}$$

As HN_3 is very soluble in the organic phase, it occurs mainly in the organic process solutions downstream of the separation column, especially in the alkaline solvent wash (as azide).

The lower explosive limit for aqueous solutions of hydrazoic acid is 17% (4.7 mol/l), high enough never to be reached under realistic Purex conditions [8]. No difficulties in plant operations have been experienced to date that are attributable to HN_3. Nevertheless, for safety reasons, knowledge of typical process concentrations of HN_3 is obligatory and, therefore, corresponding analytical efforts are necessary.

The analytical method developed at IHCH produced information on typical HN_3 concentrations in Purex process solutions for the first time [9]. This method relies on azide-selective, potentiometric measurements carried out in alkaline solution. The reactivity of HN_3 is quenched by alkalization (azide formation) so that analytical errors due to possible HN_3 reactions occurring between sampling and measurement can be avoided.

The crucial part of the method is an Ag/AgN_3 electrode prepared by anodic precipitation of N_3^- on a silver wire. Combined with a conventional reference electrode, the silver azide electrode at pH 8 exhibits activity-proportional Nernstian changes in potential (−58 mV/decade) thus permitting ion-selective, sensitive azide analyses in the range of concentrations higher than 2×10⁻⁴ mol/l (Fig. 4). The standard addition method was used in order to improve the accuracy of analysis.

If the solutions to be analyzed contain hydrazine, hydroxylamine and/or ammonium, the azide is separated by anionic exchange from the matrix and analysed in its pure form (Fig. 5). Otherwise the reaction of these constituents with silver salts would disturb the electrometric measurements.

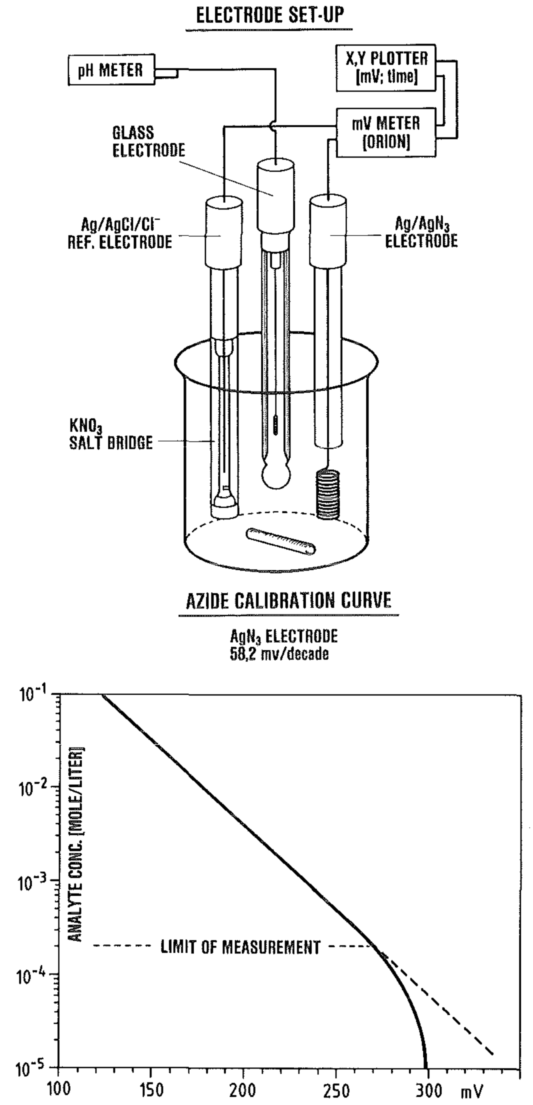

Fig. 4: HN_3 analysis

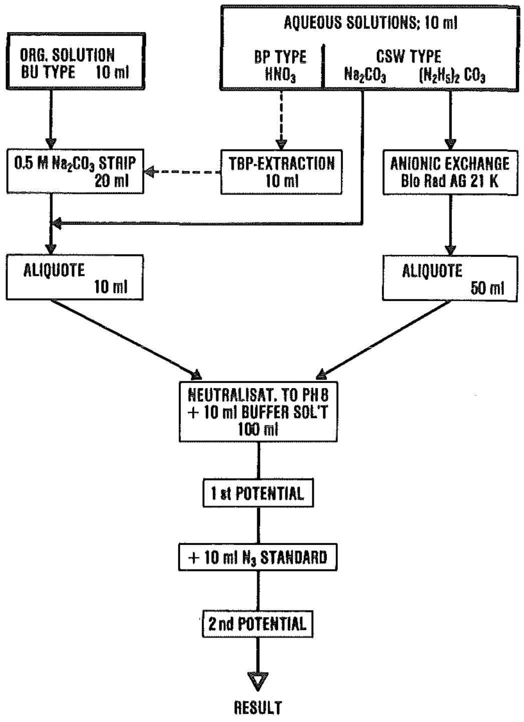

Fig. 5: Sample pretreatment for azide determination

The results obtained so far in these analytical studies show that actual HN_3 concentrations in Purex process solutions lie well below critical limits.

6. Hydroxylamine

Hydroxylamine (HAN process) has been seriously discussed as an alternative reductant to U(IV) in the Purex system. It is therefore surprising that, up to now, no specific analytical method has been developed for determination of $[NH_3OH]$ in the Purex process. The classical analytical chemical reagents Ce(IV), Fe(III) and bromate have previously been used for NH_3OH titration, but these would not work if other substances amenable to oxidation, such as Pu(III) and $[N_2H_5]^+$, were present. In this method only the "reduction potential", i.e., the sum of all reductants present, is evaluated.

We did not wish to accept this state of affairs and so we developed a HAN-specific analytical method applicable also to the boundary conditions of the Purex process [10]. The method was derived from investigations by Soviet authors [11] who had found that HAN can be oxidized quantitatively and selectively to HNO_2. We verified this finding and extended the limits of application accordingly. The nitrous acid formed can be determined very easily by spectrophotometry as described earlier.

The oxidation step is carried out by iodine in acetic acid solution. It is important in this context that HNO_2 is caught in statu nascendi by sulfanilic acid and stabilized as the diazo compound; the reaction giving the azo dye takes place later after excess iodine has been decolorized by thiosulfate. The most important criterion for applicability of the method is that hydrazine does *not* oxidize to HNO_2 under these reaction conditions.

The range of analytical measurement lies between 10^{-5} and 10^{-6} mol/l, which means that HAN concentrations above 10^{-2} mol/l typical for the Purex process, can be measured.

7. Ammonium

Only recently has the fact been recognized that Purex process solutions may contain ammonium. This actually harmless compound, which generally accompanies plutonium through the process (provided no special purification step is involved), may be the cause of precipitation in the plutonium evaporator; for instance, by reacting with HNO_2 it may produce gases in the process solutions and, eventually, give rise to disturbances in the Pu(IV)→Pu(VI) oxidation step which plays a major role in the fabrication of U,Pu mixed oxides.

Ammonium may be formed in several ways [12, 13]:

- reductive disproportionation of $[N_2H_5]^+$ according to

  $2\,Pu(IV) + 2[N_2H_5]^+ \rightarrow 2\,Pu(III) + 2\,NH_4^+ + N_2 + 2\,H^+$;

- cathodic reduction of nitric acid during U(IV) fabrication and/or by electrolytic redox techniques, respectively:

  $HNO_3 + 9\,H^+ + 8\,e^- \rightarrow NH_4^+ + 3\,H_2O$;

- technetium catalyzed hydrazine decomposition by nitrate:

  $NO_3^- + 2\,[N_2H_5]^+ \xrightarrow{Tc} NH_4^+ + 2\,N_2 + 3\,H_2O$.

In NH_4^+ analysis the conventional Kjeldahl method was initially used at IHCH. Then the more sensitive photometry involving Nessler reagent (Hg_2NI) was preferred and today we work with a commercially available NH_3

Table 2: Analysis and results in ammonium determination

Analysis

NH_3-sensitive gas-electrode (Orion) operated at pH 12; standard-addition-method

Range	$10^{-1} \ldots 10^{-5}$ mol/l
Limit of detection	ca. 10^{-6} mol/l
Precision	3% relative standard deviation

Results

- 1 BP solutions contain up to 10^{-1} mol/l ammonium
- Isolated cristalized deposits in Pu evaporator consisted of slightly soluble

  $(NH_4)_2[Pu(NO_3)_6] \cdot aq$

  and

  $(NH_4)[PuO_2(NO_3)_3] \cdot aq$

sensitive membrane electrode. Besides selectivity and sensitivity, it offers the advantage that measurements can be made even in turbid solutions without requiring preliminary separation procedures. As in azide analysis, this analysis is carried out at pH 12 using direct potentiometry and standard addition techniques (Table 2); the range of measurements is much larger than that of HN_3 analysis. One drawback is the fact that the electrometric NH_4^+ analysis is disturbed in the presence of hydrazine (these two components frequently occur simultaneously in Purex process solutions). Hydrazine must therefore be destroyed by oxidation immediately after sampling if possible, so that the disproportionation reaction mentioned earlier, which produces NH_4^+, and also decomposition of NH_4^+ by HNO_2 are ruled out. Oxidation is achieved using elemental bromine, the excessive oxidant being eliminated by Sn(II).

Acknowledgment

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On the necessity for chemical microdimensional analysis of radioactive by-products in the nuclear fuel cycle[1]

*By Franz Baumgärtner and Richard Henkelmann**

Abstract

The dissolver residues arising from delayed precipitation from light-water reactor fuel solution have been shown to consist of metal colloids. This has been revealed using photographic and X-ray fluorescence analyses of the dissolver residues incorporating high resolution electron microprobe techniques. Evaluation of a number of microparticles showed the identical chemical composition of the ε-phase, known as "white inclusions" from fast breeder fuel elements. These microanalyses also indicated that precipitates of oxidic phases of Mo and Tc, previously believed to be almost insoluble metal acids, could also have been formed as radiation-induced oxidation products of primary metallic precipitates. Moreover, segreation of colloidal silver halides has been observed in fission products, their agglomeration as microscopic AgX bodies possessing a crystal symmetry already well established macroscopically.

Zusammenfassung

Über die Notwendigkeit der chemischen Mikrobereichsanalyse bei radioaktiven Nebenprodukten des Brennstoffkreislaufs

Bei der Bild- und Röntgenfluoreszenzanalyse von Feedklärschlamm mit hochauflösenden Elektronenstrahlsonden zeigte sich, daß die Nachfällung in der Lösung von Leichtwasserreaktor-Brennstoffen aus Metallkolloiden besteht. Die Auswertung zahlreicher Mikropartikeln ergab die chemische Zusammensetzung der ε-Phase, die bei Brennelementen aus schnellen Brütern als „white inclusions" bekannt ist. Bei derartigen Mikrobereichs-Analysen ergab sich außerdem der Hinweis, daß die bisher als Ausscheidungen von schwerlöslichen Metallsäuren angesehenen oxidischen Phasen von Mo und Tc auch als strahleninduzierte Oxidationsprodukte von primär metallischen Ausscheidungen entstehen können. Weiterhin ist mit diesem Analysenverfahren auch die Segregation von kolloiden Silberhalogeniden aus den Spaltprodukten und ihre Agglomeration zu mikroskopischen AgX-Körpern mit der makroskopisch bekannten Kristallsymmetrie zu beobachten gewesen.

DESCRIPTORS

REPROCESSING
DISSOLVERS
SPENT FUELS
RESIDUES
CHEMICAL ANALYSIS
COLLOIDS
SEGREGATION
METALS
FISSION PRODUCTS
MICROSTRUCTURE
SCANNING ELECTRON MICROSCOPY
AUGER ELECTRON SPECTROSCOPY
HEAD END PROCESSES

Chemical examination of radioactive by-products in the nuclear fuel cycle, such as residues, dusts or contaminated materials of any kind, must be oriented to the chemical nature of the particular material as this may differ markedly from the chemical character of the radionuclide in question.

Therefore chemical analysis of by-products of the nuclear fuel cycle generally must provide an answer to the following two questions which are not consistent with each other:

1. Which radionuclide is it?
2. If the radionuclide is present only in trace amounts, what is the nature of the carrier material?

The first question can be answered in most cases unambiguously and without difficulty using γ-spectroscopy.

In the chemical examination of the carrier material, however, methods are often used which are similar to those normally used routinely in analyses of homogeneous inorganic substances, e. g., methods such as atomic and molecular spectroscopy, electrochemistry etc. These conventional methods of analysis only produce an integral assessment of the total sample. They do not, however, give any information on the chemical nature of the microdimensional zones. Where materials contain fission products, important information for characterization of the sample can be found only in these zones.

In this article we present the analysis of dissolver residues as an example. These residues are obtained after the dissolution of spent nuclear fuel. In accord with integral chemical analytical methods, e. g., spark mass spectrometry, emission spectroscopy, coulometry, X-ray-fluorescence etc., these residues are shown to consist of the fission product elements Zr, Mo, Tc, Pd, Ru, Rh as well as single undissolved fuel particles [1-7].

On the basis of macrochemical experience these precipitates were previously considered to be compounds of particular elements known to be difficult to dissolve in nitric acid: zirconium as oxyhydrate, molybdenum and technetium as metal acids, and the noble metals palladium, ruthenium, and rhodium in metallic form according to the energetic environment in the UO_2 host lattice.

Detailed studies on the solubility of molybdic acid and molybdenum oxyhydrate, however, led us to be sceptical of the assumption of delayed precipitations of metal acids. We therefore examined the assumption of a delayed precipitation by means of a series of single particle analyses using the scanning electron microscope (SEM) and the Auger electron spectrometer (AES). Both methods differ from the electron microprobe by the notably smaller diameter of the electron beam resulting in a resolution of 0.05 to 0.1 µm.

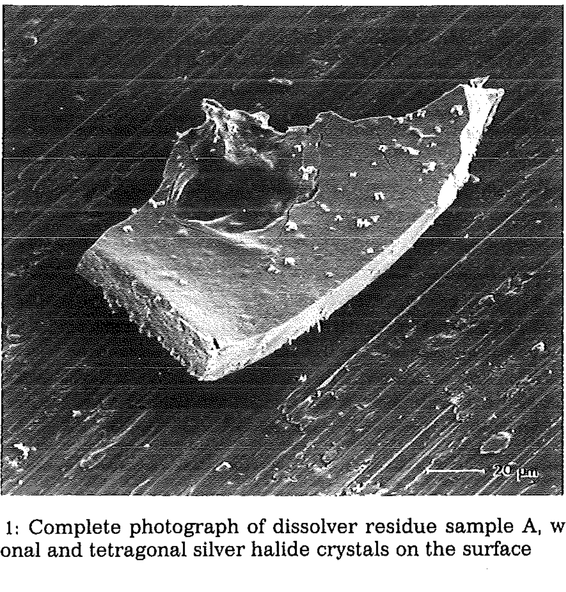

Fig 1: Complete photograph of dissolver residue sample A, with trigonal and tetragonal silver halide crystals on the surface

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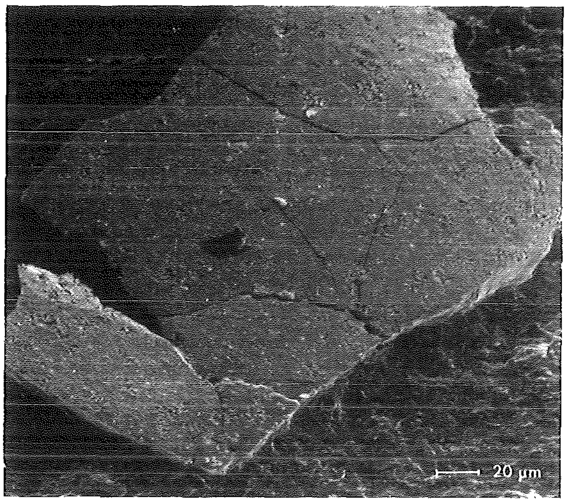

Fig 2: Dissolver residue sample B at the start of observation

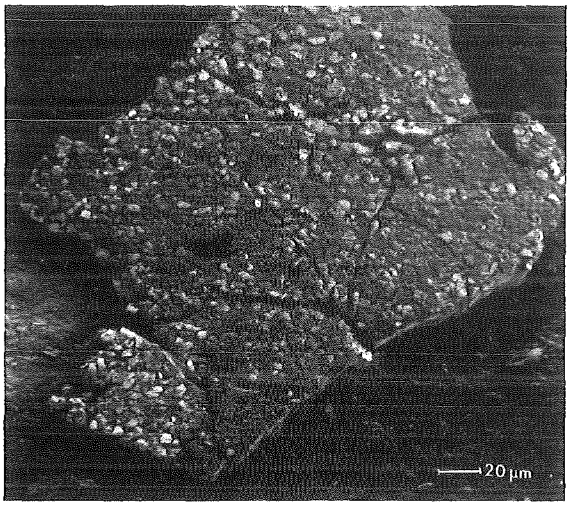

Fig 3: Dissolver residue sample B. Influence of self radiation and electron irradiation at the surface

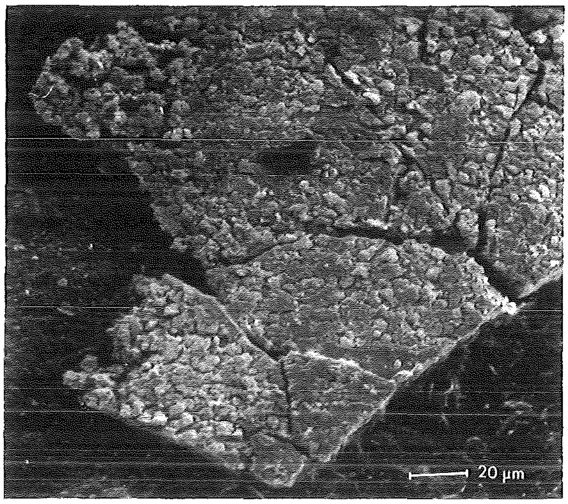

Fig 4: Dissolver residue sample B. At the end of observation the area in the upper left was intensively studied

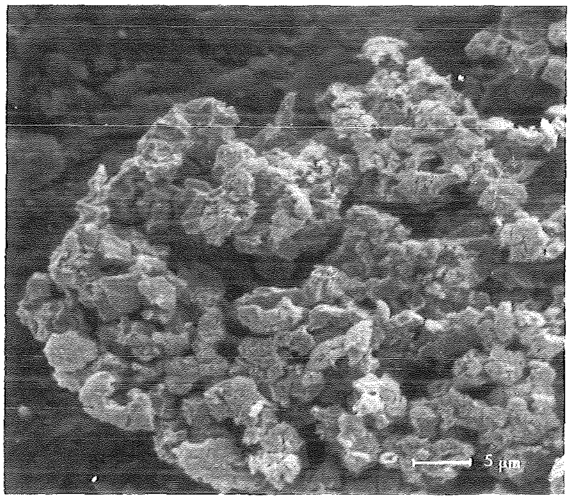

Fig 5: Dissolver residue sample B (upper left of Fig. 4). As studied by scanning microscopy

A solution of a light-water reactor (LWR) fuel with a uranium burn-up of 45000 MWd/t U was filtered several times to separate it from coarse and fine particles. On filtration after 160 hours with a Millipore filter 1 µm pores a residue was obtained which turned out with SEM and AES to be a structureless, gelatinous mass with irregular, glass-like rupture lines (Fig. 1). We interpreted this phenomenon as originally colloidal particles in nitric acid which had eventually precipitated on the filter as a gelatinous mass. A quantitative evaluation of the AES intensities showed a strongly asymmetric metal/oxygen ratio of approximately 10:1. We conclude that the gelatinous precipitate is formed from metal sols in solution.

At the surface and at rupture lines of the gelatinous material we detected coarse-structured stars of trigonal and tetragonal symmetry. Their diameter is several 100 nm while their armlength is only a few µm. A screen scan using the high resolution beam of the Auger spectrometer (about 0.05 µm) identified the trigonal and tetragonal stars unequivocally as AgBr and AgI, respectively.

Neither integral analytical methods nor the microprobe which includes a surface treatment were able to detect such microscopic heterogeneities. Thus, up to now, AgBr and AgI have never been observed as components of dissolver residues.

It appears that these microstars must have been formed rapidly, based on the small size (about 100 nm) of the irregularly shaped crystals the stars are made up of.

An explanation for the relatively rough microstructures can be seen in the metallic character of the matrix: the non-metallic silver halide submicro particles can be colloidal in nature depending on the concentration conditions and, because of their dissimilar phases, are, after filtration, fairly rapidly forced from the inside to the surface of the gelatinous metal phase. There the silver halide colloids are highly mobile and rearrange quickly into the well-known macroscopic symmetry of AgBr and AgI before the colloids of the submicrostructure have recrystallized.

Comparable microstructures and formation mechanisms have been previously observed in a study of AgBr sols, and have been characterized as "caltrop-shaped-crystals" and "Hoppercubes" [8].

Dissolver insolubles have been described up to the present as granular and crystalline material. The gradual transition from the original metallic gel to the granular structure under the influence of self-radiation and electron

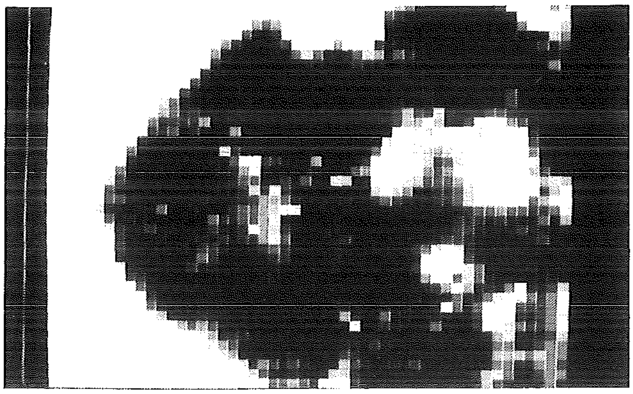

Fig 6: Distribution of technetium within the area of Fig 5, measured at the 247-eV line

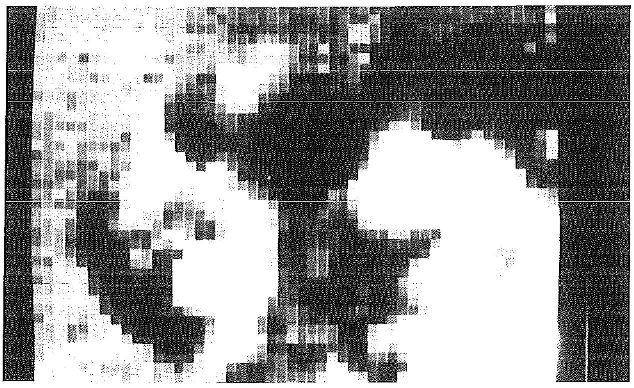

Fig 7: Distribution of molybdenum within the area of Fig 5, measured at the 186-eV line

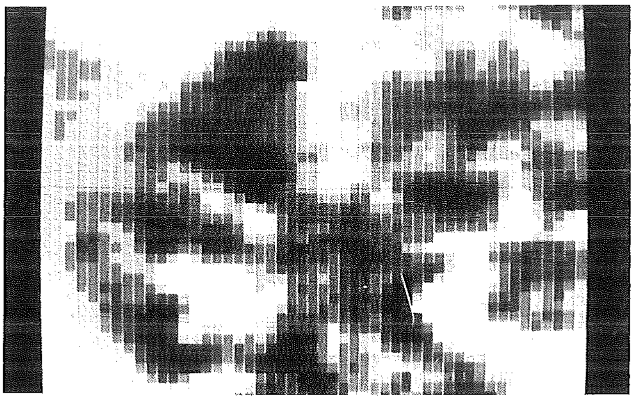

Fig 8: Distribution of oxygen within the area of Fig 5, measured at the 512-eV line

beam can be observed clearly in the Auger electron-spectrometer with its smaller beam intensity compared to the microprobe (Fig. 2 to 4). The genetic coherence between the sol-precipitate originally observed and the granular structure of the dissolver insolubles has been proven by chronological changes in their physical appearance in this microrange.

A partial segregation of elements can be detected in the granular form which must evolve from the original gel plate, since its physical shape does not change during the phase change.

A field scan of the altered, granular dissolver residue with the Auger electron-spectrometer reveals the metallic microphases to be of low oxygen content or even free of oxygen. In several areas of a granular sample containing molybdenum and technetium (Fig. 5 to 7) a field scan shows, however, a signal on the Auger line of oxygen (Fig. 8).

The observation that an originally homogeneous metal sol show oxygen-containing areas in connection with molybdenum and technetium after altering and granulation, leads to the conclusion that the metallic microranges containing molybdenum and technetium were oxidized slower afterwards. This oxidation process was, very likely, aided by the high dose rate at the surface of the sample, creating elevated concentrations of atomic oxygen radicals or ozone. The surface dose of the samples investigated was 0.35 Gy/mm^2. The dose from the electron microprobe was calculated to be 0.015 Gy/mm^2.

This study indicates again how interrelations can be overlooked by using only macrochemical methods of analysis, because these are unable to reveal the heterogeneity of microstructures.

Using high resolution microparticle analysis, our work has shown that the transition elements molybdenum to palladium are present in metal colloidal form in residues obtained from nitric acid dissolution of LWR fuel elements. This leads to the conclusion that the ε-phase known to be formed in irradiated fast breeder fuel elements is also primarily formed in LWR fuel elements. The ε-phase has so far only been demonstrated in high burn-up UO_2/PuO_2 fast-breeder fuel pins as microscopically visible metallic segregations ("white inclusions") [8].

The lower temperature and the lower concentration of fission products in LWR fuel elements (about 1 fission within a cube of 3 uranium atoms base length) would then have to be considered as the reason for the colloidal appearance of the ε-phase. In fast breeder reactors this phase has already developed microscopically visible dimensions.

Investigations similar to those described here for dissolver residues are also suggested for the application of chemical multi-element analysis with a resolution down to the submicro range, e.g., for aerosols, solvent residues, or filter fines. Such investigations have given many valuable insights into the formation mechanisms of these products.

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Radiochemical investigations on corrosion of valve metals[1]

*By G. Marx, A. Bestanpouri, W. Erben and D. Wegen**

Abstract

In order to determine the applicability of valve metals to the Purex process, the corrosion behaviour of these elements was investigated under practical conditions. For these investigations a new technique, based upon the combined application of neutron activation analysis and normal electrochemical procedures, was developed and applied to questions of particular interest. This method has the advantage that it can distinguish between the amount of material directly dissolved due to corrosion from that due to incorporation in the oxide layer. It has been proved that not only isotopic but also non-isotopic radionuclides can be successfully used for this determination. Anodic potentiodynamic and potentiostatic measurements on Hf, Ti and Ta have shown that under the practical conditions employed in the Purex process, any metal removal can be neglected. A plutonium content of up to 2.2 g/l even stabilized the oxide layer towards corrosion by forming mixed oxides of Hf and Pu. The influence of F^--ions on the stability of the oxide layer has been systematically investigated and techniques evolved for masking these corroding anions.

Zusammenfassung

Radiochemische Korrosionsuntersuchungen an Ventilmetallen

Das Korrosionsverhalten von Ventilmetallen wurde unter praxisnahen Bedingungen untersucht, um die Anwendbarkeit dieser Metalle im Purex-Prozeß sicherzustellen. Dazu wurde eine neue Methode entwickelt, die die Neutronenaktivierungsanalyse mit elektrochemischen Standardverfahren kombiniert. Sie ist in der Lage, zwischen der durch Korrosion direkt gelösten Substanzmenge und der zum Oxiddeckschichtaufbau verbrauchten zu differenzieren. Zum betreffenden Nachweis können sowohl isotope als auch nichtisotope Radionuklide dienen. Potentiodynamische und potentiostatische Messungen an Hf, Ti und Ta als Anode zeigten unter Purex-Bedingungen vernachlässigbaren Metallabtrag. Bei einem Plutoniumgehalt der Lösung bis 2,2 g/l stabilisierte sich die Oxidschicht gegen Korrosion infolge Mischoxidbildung aus Hf und Pu. Der destabilisierende Einfluß von F^--Ionen auf die Oxidschicht wurde systematisch untersucht. Es wurden Bedingungen für die Maskierung dieser korrosiven Anionen gefunden.

DESCRIPTORS

PUREX PROCESS
NITRIC ACID
VALVES
METALS
CORROSION
NEUTRON ACTIVATION ANALYSIS

1. Introduction

Valve metals are described as those metals which form a protective and non-porous layer upon exposure to air or oxidizing solutions and which also block currents while working as anodes or conduct when cathodic (albeit to various extents).

As representatives of this group the elements Al, Ti, Zr, Hf, Nb, Ta etc. are listed here. Some of them, such as Hf, Ti and to a lesser extent, Ta and Zr, have been applied to the electrochemical methods recently introduced into the Purex-process for waste minimizing. These metals or, to be more precise, their oxides are nearly insoluble in nitric acid (the Purex medium). In addition, Hf has the advantage of possessing an extremely high cross-section for thermal neutrons and can therefore act as a heterogeneous inhibitor in order to prevent criticality. A major condition for any application of these metals is their corrosion stability under practical conditions especially in the presence of plutonium. So detailed investigations were initiated into the special problems of corrosion.

The well-known Huey test, the standard method of corrosion rate determinations based upon weight difference before and after immersion into nitric acid, will fail if the weight loss by metal removal is partially compensated for by weight gain due to layer formation and if the resulting weight difference is too small to be measured accurately. Other methods usually applied to corrosion investigations are potentiodynamic and potentiostatic measurements of current densities which give information about the formation and physical properties of the oxide layer assuming that the amount of material directly penetrating into the electrolyte solution can be neglected.

Therefore a new method was developed in order to directly measure this special amount of corroded material. This technique is based upon a combination of neutron activation analysis (NAA) with corrosion measurements involving simultaneous impedance and current-density/potential measurements. Detailed information can thereby be obtained concerning the physico-chemical behaviour of these valve metals under a variety of practical conditions.

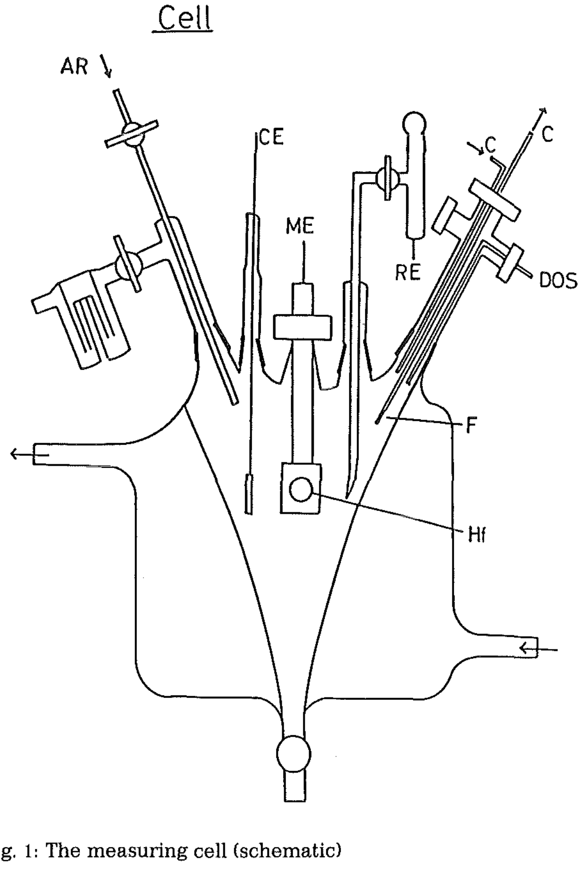

Fig. 1: The measuring cell (schematic)

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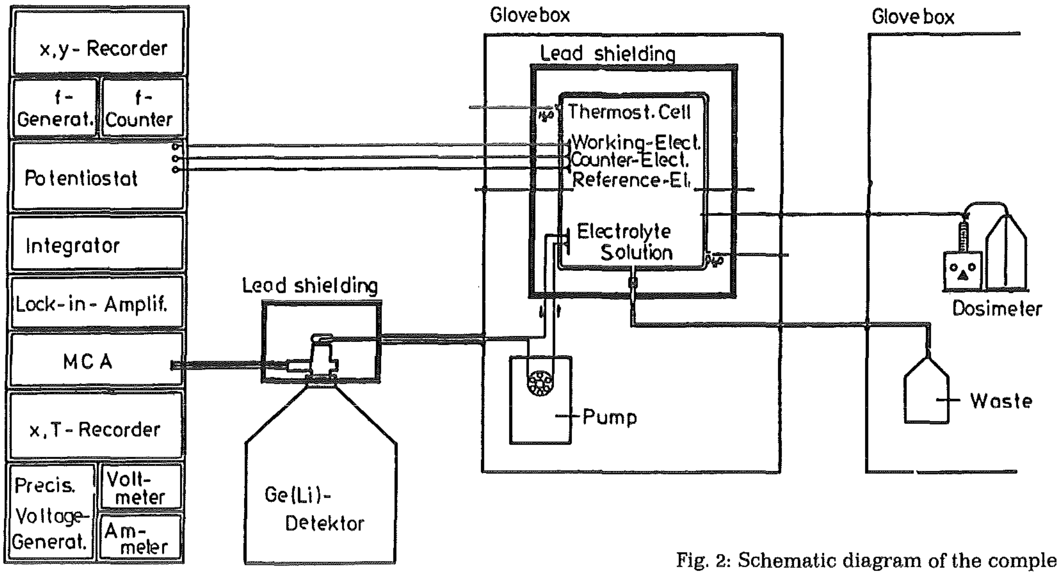


Fig. 2: Schematic diagram of the complete apparatus

2. Experimental details of the electrochemical method

2.1. *Anodic potentiostatic measurements of valve metals*

A schematic illustration of the glass cell and the apparatus used for the electrochemical investigations of corrosion can be seen in Figs. 1 and 2. The metal to be investigated acted as the working electrode (ME). Gold was the counter electrode (CE, 2 cm^2 cross-section) and Hg/Hg_2SO_4 in 1 N H_2SO_4 the reference electrode (RE), which was in contact with the electrolyte solution via a Luggin capillary. This arrangement was employed in order to prevent corrosive ions from moving to the working electrode. On the other hand, a major disadvantage which could not be avoided was that HNO_3 diffused into the electrode compartment thereby changing the concentration of the reference system. A new type of Ag/AgCl electrode system recently introduced prevented any Cl^--ions from entering the cell compartment. These electrodes were successfully applied to all systems under investigation.

Gases introduced through various inlets were employed for stirring the solution and preventing the intrusion of O_2. They were also used for the solution cycle and served the counting equipment (C).

The cell was equipped with double walls for thermostating purposes. Measurements at higher temperatures required the removal of the reference electrode from the cell compartment. All the potentiostatic experiments were registered with an *x,y* chart recorder. The solutions were transferred continously from the cell to a cuvette by a peristaltic pump.

Voltmeters and ammeters provided rapid and continuous measurements of the data required. The precision voltage generator compensated for the potential of the reference electrode, thus permitting the polarisation voltage to be compared directly with that of the normal hydrogen electrode.

A lock-in amplifier and a frequency generator were used for determining the impedance at various frequencies (i.e., the capacity), thereby simultaneously monitoring the thickness of the oxide layer and the current-potential characteristics.

2.2. *Anodic potentiodynamic measurements of valve metals*

Important current-density/potential characteristics can be obtained from potentiodynamic measurements, which give an insight into the mechanism of formation of the oxide layer.

Preliminary investigations have shown that three different ranges of the rate of polarization have to be considered. With rates higher than 1 V/s the system does not respond simultaneously and similarily with rates lower than 1 mV/s the results obtained from cathodic measurements are not reproducible. On the other hand no difficulties are observed in the anodic range apart from long experimental times.

The most suitable rate for high-frequency investigations proved to be 50 mV/s. The valve metal was polarized by a DC triangle produced by a generator in which the maximum could be increased in steps of 0,5 V, until local corrosion was noticed by a rapid increase in current density (see Fig. 3). During polarization, the current

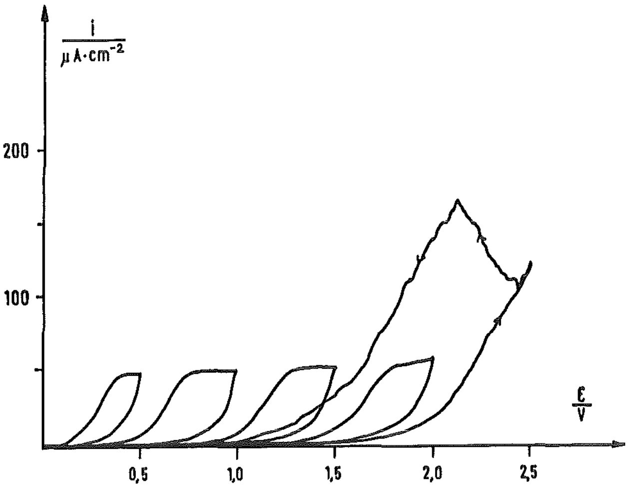


Fig. 3: Current-density/potential plot of hafnium in 5 M HNO_3 at 20 °C

density was simultaneously monitored, thereby giving the total charge and enabling the direct corrosion to be calculated.

The samples' surfaces were cleaned before investigation. In general, the activated valve metal sample was fixed to its sample holder and then dipped into a solution, consisting of 1 part of 40 % HF, 4 parts of 65 % HNO_3 and 5 parts of water, for 15 s in order to completely remove any oxide layer present. It was then carefully rinsed with bidestilled water, placed in the cell and connected to the potentiostat. The current increased immediately, indicating the formation of a primary oxide layer before decreasing very slowly towards zero. After transferring the cell contents to the cuvette as described previously, the radioactivity was measured at 10-minute intervals. The constant value eventually reached was taken as background. After each voltage triangle the activity was again measured until a constant value was obtained.

3. Experimental details of the radiochemical method and its applicability to corrosion measurements

The apparatus used for radiochemical measurements consisted either of a Ge(Li) detector or of a NaI(Tl) scintillation counter combined with a multichannel (MCA) or single-channel analyzer (SCA). A cuvette was placed in front of the detector, through which the cell contents were continuously pumped. The amount of electrode material directly dissolved as a result of corrosion was calculated from the concentrations of the specific radionuclides present in solution. These radionuclides were obtained from (n,γ) reactions and also from (n,p) and (n,2n) reactions. Special attention is drawn to the non-isotopic detection of titanium and nickel.

Two questions arise: (1) can sorption phenomena erroneously affect the results, (2) does scandium, for example, truly indicate the corrosion behaviour of titanium.

In reply to (1), radioisotope exchange experiments and a comparison of electrochemical and radiochemical data have shown that no unexpected sorption occurs.

In order to answer (2) the solution was first analyzed radiochemically for Sc-46 followed by an atomic absorption spectroscopic analysis (AAS) of titanium (see Tables 1 and 2). The results were studied over the total amount of reacting material, which was derived from the electrochemical reaction and the exact quantity of Ti directly dissolved from corrosion. Within error limits the ratios obtained were identical. Identical results were obtained from polarographic and γ-spectroscopic measurements of Ti and Sc-46 or Sc-47 (see Table 3). In addition, a variety of different analytical procedures (radiochemical methods, quantometric analysis and AAS) were used to analyze a special type of stainless steel (1.4306 N).

These results (Table 4), agreeing well with earlier work and with DIN data, show that both isotopic and non-isotopic tracers can be used for the investigation of corrosion phenomena, a fact which has often been questioned by electrochemists unfamilar with radiochemical methods.

Table 1: Gamma-spectroscopic measurements of titanium
Tracer Sc-46

Time of Polariz.	concentration		
t_p / min	c_{el} / ppm	c_γ / ppm	c_{el}/c_γ
61	3.7	6.6	0.6
60	3.4	4.1	0.8
62	4.0	6.0	0.7
59	3.0	5.3	0.6

Table 2: Atomic absorption spectrometric measurements of titanium
$U_H = -230$ mV, 1 N HNO_3, 710 ppm Hf

Time of Polariz.	concentration		
t_p / min	c_{el} / ppm	c_{AAS} / ppm	c_{el}/c_{AAS}
58	3.5	6	0.6
78	5.2	6	0.9
60	4.5	7	0.6
64	3.9	7	0.6

Table 3: Comparison of electrochemical with radiochemical methods

	polarographic	γ-spectroscopic		
V / ml	$c_{Ti^{4+}}$ / $g \cdot l^{-1}$	c_{Sc-47} / $g \cdot l^{-1}$	$c_{Sc-46(889)}$ / $g \cdot l^{-1}$	$c_{Sc-46(1120)}$ / $g \cdot l^{-1}$
0.5	$(9 \pm 1) \cdot E^{-4}$	$(9 \pm 1)E^{-4}$	$(9.3 \pm 0.2)E^{-4}$	$(9.5 \pm 0.3)E^{-4}$
1.0	$(1.7 \pm 0.1)E^{-3}$	$(1.8 \pm 0.2)E^{-3}$	$(1.81 \pm 0.04)E^{-3}$	$(1.86 \pm 0.06)E^{-3}$
1.5	$(2.5 \pm 0.1)E^{-3}$	$(2.7 \pm 0.3)E^{-3}$	$(2.65 \pm 0.06)E^{-3}$	$(2.72 \pm 0.08)E^{-3}$
0.5	$(9 \pm 1)E^{-4}$	$(9 \pm 1)E^{-4}$	$(9.1 \pm 0.2)E^{-4}$	$(9.2 \pm 0.3)E^{-4}$
1.0	$(1.7 \pm 0.1)E^{-3}$	$(1.7 \pm 0.2)E^{-3}$	$(1.77 \pm 0.04)E^{-3}$	$(1.80 \pm 0.06)E^{-3}$
1.5	$(2.4 \pm 0.1)E^{-3}$	$(2.5 \pm 0.3)E^{-3}$	$(2.59 \pm 0.06)E^{-3}$	$(2.63 \pm 0.08)E^{-3}$

Table 4: Results of various analytical methods applied to stainless steel (1.4306 N)

	DIN 17440	Radiochem.	Quantometer	AAS
Fe	Rest (70-65%)	67.0%	Rest (67.5%)	68.0%
Cr	17-20%	18.5%	19.2%	18.5%
Ni	10.5-12.5%	11.4%	11.0%	11.1%
Mn	≤ 1.0%	ca 1.5%	1.50%	1.43%
Mo	≤ 0.4%	0.39%	0.38%	0.35%
Si	ca 1%		0.41%	
N_2	≤ 0.22%			
C	≤ 0.03%		0.025%	
S	≤ 0.02%		0.012%	
P	≤ 0.02%		0.026%	
Co	-			0.21%

AC impedance measurements can also be employed to show that the activation procedure itself will not influence corrosion behaviour, even if the valve metals under investigation are irradiated with a high neutron flux density (ca. 10^{14} $cm^{-2}s^{-1}$) for a long period of time (1000 h). As can be seen from Fig. 4, the sensitivity of the radiochemical determination lies between 10^{-4} and 10^{-10} mol/l and depends primarily upon the neutron cross sections of the various elements to be activated and the incident neutron flux density.

Supplimentary to these data, isotopic abundances, irradiation times and the time intervals between the end of the irradiation and the start of the investigations must also be taken into account. The well-known activation equation produces linear calibration curves, so that the application of a full log plot will result in parallel slopes for all activations, transferring fluctuations in the neutron flux densities and all irregularities of the irradiation to the abscissa. It is therefore not necessary to determine a calibration curve for each activation. The only requirement is the simultaneous irradiation of a known standard in order to determine the y-shift in the calibration curve. In the presence of plutonium a Ge(Li)-detector and an MCA are required for the radiochemical measurement of corrosion, as may be seen from Fig. 5.

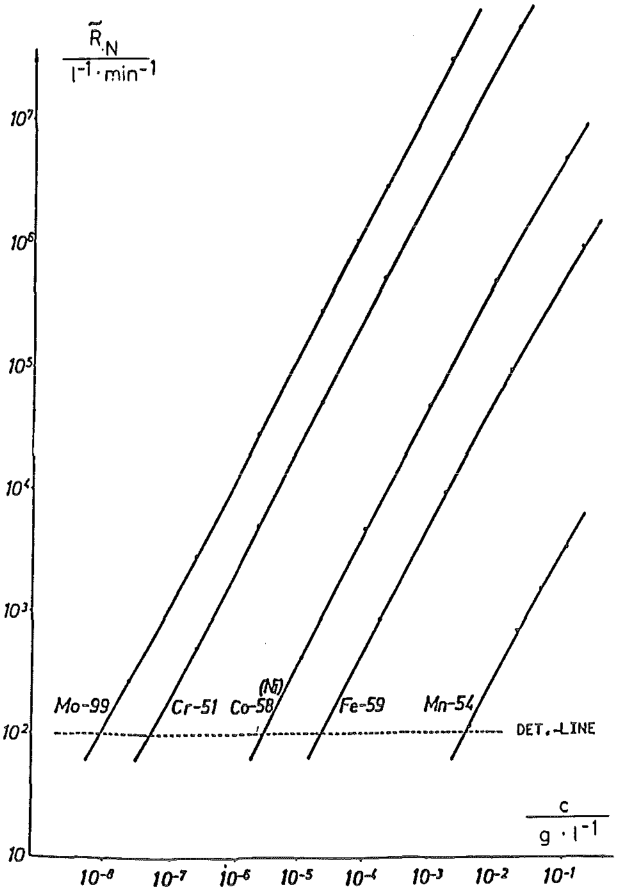


Fig. 4: Calibration curve of stainless steel

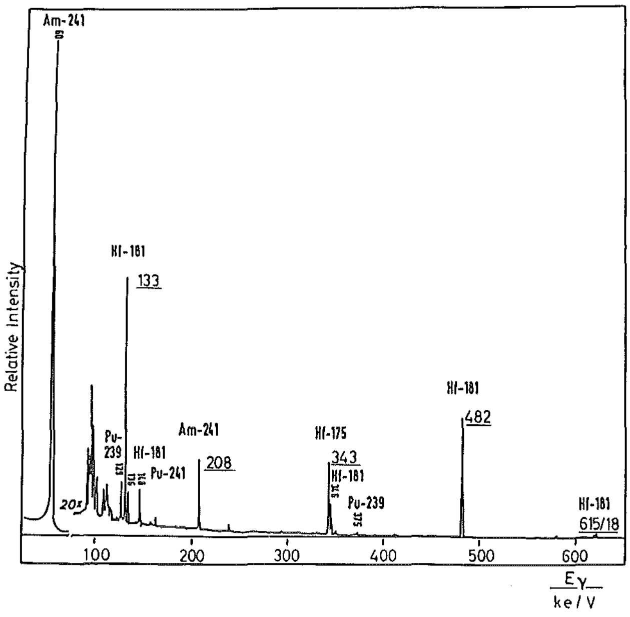


Fig. 5: Ge(Li) spectrum of Hf in presence of Pu

The Hf-181 and Hf-175 peaks may be clearly distinguished, whereas the Pu peaks and those of Am-241 (produced by the β-decay of Pu 241, a constituent of reactor plutonium) are to be found at lower energies. Investigations carried out on the various valve metals in the absence of plutonium have been completed using SCA facilities alone.

4. Results and discussion

4.1. Anodic potentiostatic measurements of hafnium

The results of long-term potentiostatic experiments with pure Hf and technical grade Hf at +2 V and 20 °C in pure HNO_3 can be seen from Table 5. As expected, the corrosion rate was low with the exception of the 0.5 M solution. The fraction of the total turn-over due to corrosion for this solution is also significantly higher. This higher corrosion may occur because the oxidation potential of the dilute acid is not high enough to stabilize the surface oxide layer. Table 5 also gives results for the same acids but with the addition of 2.2 g/l Pu(IV), which corresponds to a Purex medium. Until now, it was suspected that α-radiation would destroy, or at least damage, the oxide layer of Hf, thereby leading to increased corrosion. The experimental results contradict this hypothesis; there is no increase in corrosion. On the contrary, a significant reduction in corrosion rate could be observed in the case of the 0.5 M HNO_3 solution.

The next step was to look at the surface layer itself using the XPS Facility of the Euratom Institute for Transuranium Elements at Karlsruhe. A Hf sample was investigated which had been polarized in HNO_3 solution in the presence of plutonium. Unfortunately the isolation property of the oxide broadened the half widths of the Pu 4f peaks, so that it was impossible to distinguish between the peak positions of Pu(III) and Pu(IV). The only difference between these peaks were the small shoulders at the base of the Pu(IV) peak. From previous corrosion measurements where plutonium was shown to exert an influence, significant amounts of plutonium were expected to be found in the oxide layer. In fact the amount found was at the lower limit of detection, only 1.5%, corresponding to 10 mg plutonium per m^2 of Hf surface.

Nevertheless it could also be shown that the surface was free of nitrate and that plutonium was present as the dioxide, the latter forming a mixed oxide with HfO_2 and not just an oxide mixture. Upon sputtering with Ar, Pu(III) oxide was produced, which, in contrast to Pu(IV), existed as discrete crystals within the host matrix. As the intensity of the plutonium peak did not decrease with sputter time it is believed that the PuO_2 was not concentrated at the surface but homogeneously distributed throughout the entire layer.

Finally the spectrum obtained by X-ray photoelectron spectroscopy (XPS) from an Hf-foil dipped into a fast breeder fuel solution indicated that whereas Pu(IV) was incorporated into the oxide layer this was not true for U(VI), probably because the dumb-bell shaped uranyl-ion could not fit into the HfO_2-lattice.

The next investigation of the surface layer was by AC impedance measurements. For this special case, the polarizing DC triangle was modulated by a very small AC signal, the response of the system being registered with a lock-in amplifier. Applying this versatile method it is hoped that information may be obtained by an independent measurement not only concerning the thickness of the oxide layer but also its dielectric constant and its polarization resistance. For this purpose the low measurement frequency range has been extended in order to obtain the polarization resistance and to enable the calculation of the corrosion rate using fast Fourier transformation analysis. The thickness and dielectric constant of the oxide layer are related via the capacity. While thickness is determined by the polarization potential it is also influenced by the resistance of the layer. The Bode plot shows a significant difference between pure HfO_2 and plutonium doped oxide, despite the fact that in the bulk, both are insulators. It therefore seems that the dielectric constant of the mixed oxide shows a different frequency dependence. It will require further investigation to see if the present hypothesis of a substoichiometric PuO_2 can explain these effects.

Long-term potentiostatic measurements at +2 V and at 20 °C show that Pu(III) has no significant influence either upon the corrosion behaviour of pure Hf or of technical grade Hf (see Table 5) in 0.2 to 1 N HNO_3. This relatively low acid concentration was chosen in accordance with Purex conditions for separating plutonium from uranium by electrochemical reduction. The results are similar to those obtained in the presence of Pu(IV). Direct dissolution through corrosion is approximately 3 % and independent of HNO_3 concentration. The metal removal rates, which are also not influenced by HNO_3 content, are in the range of a few µm/a (see Table 5).

Table 5: Potentiostatic polarization of hafnium
Long-term (20 h) potentiostatic polarization at +2 V, temperature 20 °C

ELECTROLYTE SOLUTION	C_{HNO_3}	TECHN.Hf(97% KfK)		PURE Hf(99,5%, HEK)	
		Maximum Value	Mean Value	Maximum Value	Mean Value
PURE NITRIC ACID	0.5M	71	51	67	67
	1-5M	17	8	7	4
WITH ADDITION OF 2.2g/l Pu(IV)	0.5M	7	7	9	7
	1-5M	14	6	5	3
WITH ADDITION OF 2.2g/l Pu(III) 0.2g/l HYDRAZINE	0.2-1M	2	2	2	2

Pu(III) also has a stabilizing effect on the HfO_2-layer although it does not form any mixed oxides. This behaviour results as a consequence of the immediate oxidation of Pu(III) to Pu(IV) at the Hf-anode, thereby emphasising that only Pu(IV) is incorporated as described earlier.

4.2. The influence of fluoride ions upon hafnium corrosion

In practice, the presence of a small amount of F^- in the ppm range in fuel elements cannot be avoided. This results firstly from their manufacture from UF_6 and secondly from the nuclear reaction

$$^{18}O(n,\gamma)\,^{19}O \xrightarrow{\beta^-} {}^{19}F,$$

which occurs in the reactor.

As was first shown by *R. Droste* [1], a member of our team, Hf corrosion increased with increasing F^- content (e.g., 4.5 mm/a at 100 ppm F^- and 0.6 mm/a at 20 ppm F^-, cf. Fig. 6). F^- influence on corrosion can however be drastically reduced upon the addition of Zr^{4+} ions. As may be seen from the data, the F^- ions are completely masked by Zr^{4+} ions as long as there are sufficient Zr^{4+} ions present in solution to form the complex ZrF^{3+}. The formation of other Zr-F complexes with lower Zr-F ratios also reduces the Hf corrosion rate but not so efficiently while a higher Zr-F ratio has little influence on corrosion behaviour. In the presence of F^- ions, the HNO_3 concentration has no effect on Hf corrosion.

4.3. Anodic potentiostatic measurements of titanium and tantalum (including investigations at zero current)

As mentioned previously, the behaviour of Ti towards corrosion can be investigated using the non-isotopic tracers Sc-46 and Sc-47. Table 6 shows the results of some corrosion measurements at equilibrium obtained from the radiochemical method at various HNO_3 concentrations. For these investigations Ti samples activated by neutron irradiation were monitored for various times with an Ag/AgCl electrode as reference. The voltage was continuously measured by an impedance converter connected to an x,t recorder. The integral, linear and specific metal removals were also measured over the time interval from 0 to 10 hours, results indicating that they could be neglected (< few µm/a).

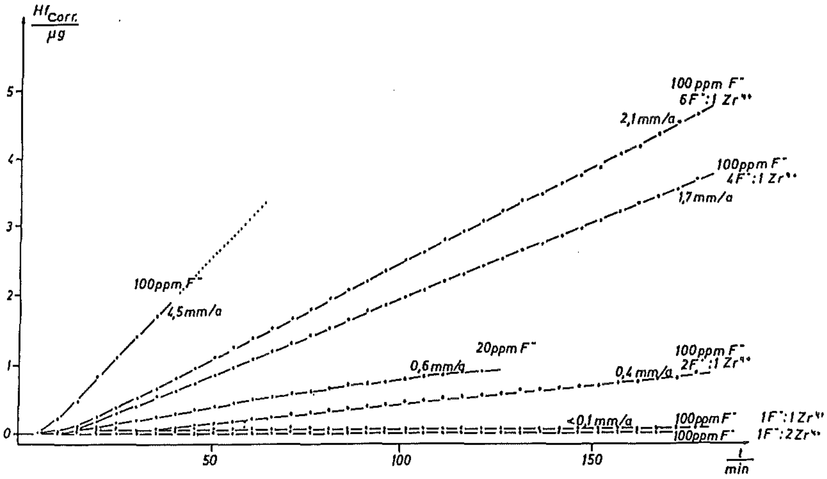


Fig. 6: Masking effect of Zr^{4+} on F^-

The corresponding results for anodic polarization over 20 hours at 20 °C can be seen in Table 7. At the various HNO_3 concentrations the polarization voltages ranged from higher to lower values than that at the specific equilibrium state. Even under these special conditions the linear and integral removals were found to be in the range of a few µm/a, the current density being negative at the lower voltage.

Table 6: Titanium corrosion rates at 20 °C

c_{HNO_3} / $mol \cdot l^{-1}$	U_R / mV	t / h	$W_{lin.}$(0-10h) / $\mu m \cdot a^{-1}$	$W_{lin.}$(>50h) / $\mu m \cdot a^{-1}$	$W_{int.}$ / $\mu m \cdot a^{-1}$	m / µg
1	370±10	250	1.2±0.9	0.5±0.2	0.7±0.1	4.7±0.6
5	930±30	150	4 ± 3	0.8±0.6	2.1±0.5	9 ± 2
8	860±30	100	2 ± 5	1 ± 3	2.0±0.3	4.9±0.7

Table 7: Anodic polarization of titanium for 20 hours at 20 °C

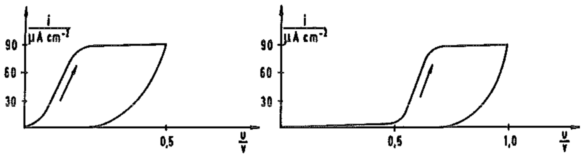
c_{HNO_3} / $mol \cdot l^{-1}$	U_p / V	i / $\mu A \cdot cm^{-2}$	$W_{lin.}$(>10h) / $\mu m \cdot a^{-1}$	$W_{int.}$ / $\mu m \cdot a^{-1}$	m / µg
1	0		2.4 ± 0.8	4 ± 2	2 ± 1
1	+ 0.5	+ 0.1	2.9 ± 0.5	5 ± 1	2.5± 0.6
5	+ 0.5	- 14	4 ± 2	6 ± 6	3 ± 3
5	+ 1	+ 0.5	2.2 ± 0.8	5.7±0.5	3 ± 0.3
8	+ 0.5	-229	2.4 ± 0.8	5 ± 1	2 ± 0.5
8	+ 1	+0.02	2.8 ± 0.6	7 ± 2	3 ± 1

Similar results were also obtained from anodic potentiostatic measurements with Ta under various practical conditions. For this special valve metal it should be emphasized that no material is dissolved directly by corrosion, but that the whole current flow is used in oxide layer formation. From the anodic point of view and considering only corrosion, it should be noted that this is the most resistant valve metal.

It should be remembered that all results obtained from potentiostatic measurements are only valid for anodic polarization and in the presence of plutonium at contents up to 2.2 g/l. Further investigations will indicate the corrosion behaviour of valve metals at higher Pu contents (up to 200 g/l) especially under cathodic conditions.

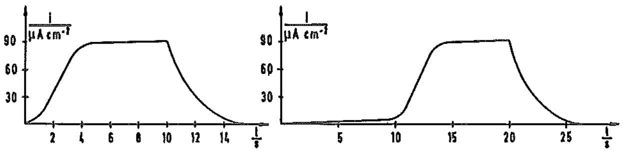
4.4. Anodic potentiodynamic measurements of valve metals

The importance of potentiodynamic polarization experiments for understanding the effects which occur at the electrode cannot be over-emphasized. An insight into the nature of the oxide layer can be obtained from the characteristic slope of the voltammetric curves (see Fig. 7). An initial inactive range (range 1) may be observed, followed by an increase in the current (range 2) leading to a range of constant current density before finally returning to the starting point (range 4). Within range 1 there is no noticeable current flow and no metal removal. In this initial range the existing oxide layer remained unchanged. Upon increasing the potential a current begins to flow, which partially contributes to extending the thickness of this oxide layer and partially to corrosion by direct dissolution (range 2). For a particular metal the ratio of these two effects depends upon the electrolyte composition and the voltage applied. It is possible to assess the polarization resistance from the gradient of the slope for this region, this slope demonstrating that in this range corrosion is dominant. In range 3 the current density remains constant. Here corrosion plays only a minor part, the current being mainly used for increasing the thickness of the oxide layer, an event which is diffusion-limited. The thickness of the layer is proportional to the voltage applied, which is typical for all the valve metals. Returning to the starting point (range 4) produces a further increase in the thickness of the oxide layer and also changes in the charge of the electrical double layer, two effects which cannot be easily distinguished. No significant metal removal is noticeable in this range.



i-U-curve 0,5V

i-U-curve 1,0V



i-t-curve 0,5V

i-t-curve 1,0V

Fig. 7: Current-potential characteristics of Hf

In the voltage range from 3 to 5 V non-reproducible local corrosion of Hf occurs. This is indicated by an increase in the current density up to 400 µA/cm², the statistical current changes being due to spontaneous corrosion and repassivation. In HNO_3 the repassivation of Hf is dominant compared with its local corrosion, whereas the opposite is true in the presence of Cl^- ions, for example. This behaviour seems to confirm the theory of the destruction of the oxide layer by anions.

At higher voltages this procedure cannot be reproduced and the electrode behaves in the same way as at the beginning, showing the characteristic curves indicating local corrosion to be restored by repassivation. However this local corrosion does not decrease the usefulness of Hf in nuclear technology. Using long-term polarization it is possible to exclude any local corrosion. This can be achieved by extending the potentiodynamic polarization up to a point directly below the potential of local corrosion by polarizing the electrode at this voltage for at least 20 to 100 hours. This procedure makes the electrode inert to local corrosion at potentials up to 100 V and more.

The same results were also obtained from measurements carried out in the presence of Pu.

This behaviour under potentiodynamic conditions may possibly be explained by the formation of an amorphous oxide layer consisting of hydrated hafnium oxide which becomes more crystalline under long-term polarization, forming a layer of higher resistance towards corrosion.

It should be stressed that, by investigating the behaviour of valve metals from potentiodynamic measurements alone, incorrect conclusions cannot be avoided. To obtain answers relative to the usefulness of those materials in the field of nuclear technology it is necessary to carry out potentiostatic investigations.

Acknowledgments

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Decontamination in light-water reactors, techniques and experiences[1]

*By K. H. Neeb**

Abstract

The chemical and electrochemical processes currently available for decontamination in light-water cooled nuclear power plants are reviewed and examples for application are given. The paper points out that the process to be used has to be chosen according to the special problem and that there is no process for general use. Quality assurance of the process is of paramount importance, especially concerning decontamination effectiveness and absence of possible harm to the integrity of the materials present.

Zusammenfassung

Dekontamination in Leichtwasserreaktoren, Verfahren und Erfahrungen

Die derzeit für Dekontamination in Leichtwasserreaktoren verfügbaren chemischen und elektrochemischen Verfahren werden kurz beschrieben. Beispiele für ihre Anwendung werden angeführt. Die Darstellung zeigt, daß das anzuwendende Verfahren auf die jeweils vorliegende Aufgabenstellung zugeschnitten sein muß, daß es daher ein allgemein verwendbares Verfahren nicht gibt. Von besonderer Wichtigkeit ist die Qualitätssicherung der Verfahren, vor allem hinsichtlich Dekontaminationswirksamkeit und Unschädlichkeit für die Integrität der vorliegenden Werkstoffe.

1. Introduction

The contamination of systems and the radiation exposure to persons caused by it are an undersirable but inevitable phenomenon in nuclear plants. Reduction can be achieved by suitable steps:

Personnel exposure at a given dose rate may be limited by

- appropriate plant design,
- high quality of materials and construction resulting in low requirements for inspection and repair,
- as far as possible by application of remotely controlled devices for inspection, examination and required repair work.

Measures necessary for reduction of dose rates in light-water cooled nuclear power plants are

- use of highly corrosion-resistant materials with as low as possible content of elements forming long-living and gamma-emitting radionuclides under neutron irradiation,
- maintaining water chemistry which, apart from mininum corrosion attack, results in low corrosion product transport,
- decontamination of components, systems and circuits as a preparation for work requiring extensive manpower.

By combining these measures personnel radiation burdens in German nuclear power plants have been kept well below the regulatory limits.

The actual state of decontamination techniques used in light-water cooled reactors and the experience gained during their applications are summarized below.

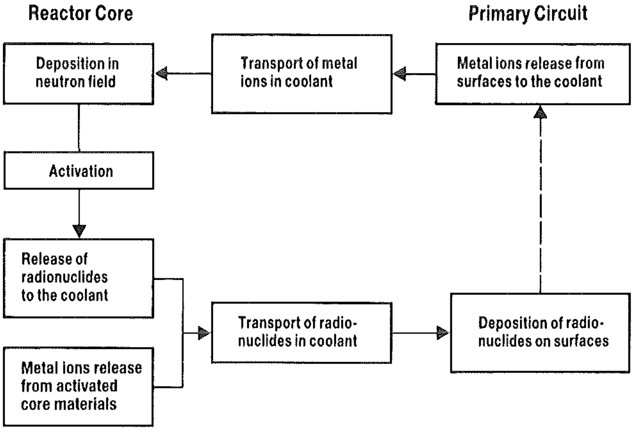

Fig. 1: Mechanism of contamination build-up in the primary coolant loop of a pressurized water reactor (schematic)

2. Nature and build-up of contamination layers in light-water reactors

Contamination in light-water reactors is caused by neutron activated corrosion products, mainly ^{60}Co and, to a minor extent, ^{58}Co and ^{54}Mn; fission products contribute only in special cases. As shown in Fig. 1 two different mechanisms may be responsible for contamination build-up. Primary sources in one case are Co impurities in corrosion products, which are transported by the coolant to the neutron field where they become activated. In the other case, the primary sources are corrosion products released from highly activated materials located within the neutron field. The radionuclides generated in this way are transported by the 300 °C coolant, partly in the dissolved state and partly as suspended matter, to the primary circuit, where they can be incorporated into the oxide layers present on the surfaces of the materials. Details of the reaction mechanisms leading to incorporation are not very well understood up to now.

In PWR primary circuits the oxide layers consist of Cr- and Ni-containing magnetite-type oxides (Fe_3O_4). Layer thicknesses are normally very small (around 0.5 µm), the layers are strongly adhering to the base metal, so it is very difficult to remove them by mechanical means. In boiling water reactors (BWR) the comparatively high oxygen content in the reactor water leads to oxide layers which, in the extreme case, are composed of pure hematite Fe_2O_3. In both cases, the oxide layers have a very dense structure, thus providing an effective barrier against high-temperature water corrosion.

In addition, activated corrosion products are transported by water to the auxiliary systems, where they settle in pipes, vessels, etc., in a loosely adhering form and may be removed by mechanical means.

3. Decontamination techniques and their application

3.1. General

The aim of decontamination is to remove radioactivity from the base metals of circuits and components. To achieve this, appropriate techniques have to be used, and the problems to be faced may show very different aspects: the object of a particular decontamination may be reduction of dose rates in preparation for maintenance or repair of components for re-use; or it may be decontamination of materials prior to their disposal. In any case the procedure must ensure a sufficiently high decontamination factor. The procedure applied to components for re-use must not damage the base materials. This very important condition, which will be discussed later, does not apply to decontamination before scrapping. Moreover,

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[1] Revised from a paper presented at the winter seminar on new developments in the field of reprocessing. Obertraun, Austria, March 4-10, 1984, organized by the Institut für Heiße Chemie, Kernforschungszentrum Karlsruhe, in collaboration with Gesellschaft Deutscher Chemiker and Gesellschaft Österreichischer Chemiker.

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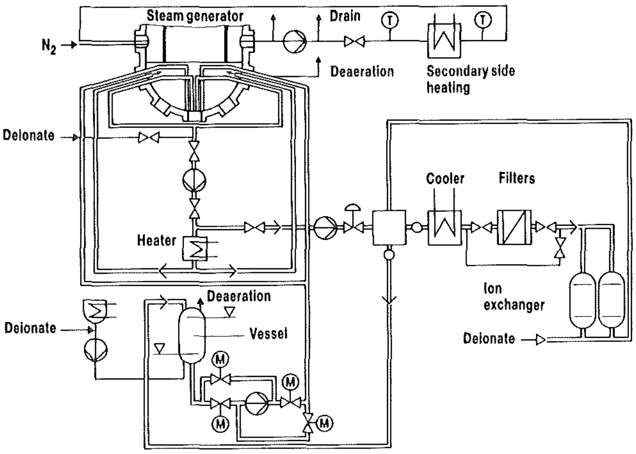

Fig. 2: Decontamination of the steam generators channel head in a pressurized water reactor; engineering flow-sheet

the decontamination procedure used must take into account the nature of the oxide layers present as well as the materials under consideration; changes and effects occurring to both of them during their operational histories are specially important. This means that no general decontamination procedure can be applied in all cases.

Another important aspect is the question of carrying out the decontamination process. Apart from economic considerations there are important questions relative to the space necessary for the relevant installations, access to the systems to be decontaminated and radiation exposure of individuals. Finally, the residual contaminated solutions should have as low a salt concentration as possible in order to avoid subsequent problems in waste handling.

The following two Sections concentrate mainly on chemical and electrochemical decontamination techniques. For the sake of completeness it should be mentioned that non-chemical techniques (e.g. high-pressure water lancing, sand blasting) are also used, but mainly for removal of comparatively loosely adhering contamination.

3.2. Chemical procedures

In chemical decontamination the contaminated oxide layers are mostly dissolved by suitable agents. Organic complexing agents such as dicarbonic acids have generally proved to be the best choice, particularly as regards oxide solubility and compatibility with base metals.

Contaminated layers on *non-alloyed and low-alloyed steels* which consist more or less of pure iron oxides are rather easily soluble in those complexing agents, thus making possible a one-step procedure. As an example the CAPA (*C*itronensäure-*A*meisensäure-*P*assivierung) process developed by KWU should be mentioned here. This process, which gives good oxide dissolution, also simultaneously repassivates the decontaminated metal surfaces. In BWR main steam lines decontamination factors (DFs) of 5–10 have been obtained by this process.

In contrast to this, the oxide layers on *austenitic steels* contain significant amounts of chromium and nickel so that complexing agents produce only a very limited effect. With those oxides a pretreatment step must be used to create active centers as starting areas for complex formation. Because of the different nature of the oxide layers mentioned in Section 2, pretreatment can be carried out in two different ways:

With PWR oxide layers of the Cr- and Ni-bearing Fe_3O_4 type, oxide pretreatment should be strongly oxidizing in order to convert Cr(III) present into water-soluble Cr(VI). Usually, permanganate solution is used for this purpose; after reduction of excess MnO_4^- to Mn^{2+} both the radionuclides responsible for contamination and the iron oxides are dissolved by dicarbonic acids (e.g. oxalic or citric acid). Most pretreatments and complex formation are carried out at temperatures of 90 to 100 °C; with temperatures above 100 °C higher DFs are obtained as is done in one of the well-known decontamination processes, but this requires more expensive technical procedures using overpressurization.

The best known example of these two-step decontamination processes including preoxidation is the APAC process (Alkaline Permanganate Ammonium Citrate) [1], which has since been modified several times. Based on this process, KWU has developed the MOPAC process (Modifizierter APAC) which, in order to obtain a more effective protection of the base metals, uses an inhibitor as well as varied dicarbonic acid composition. MOPAC is especially appropriate for decontamination of components with limited dimensions [2]. Practical experience with this process, which has been used in the decontamination of approximately 40 PWR main coolant pump impellers, 6 pressurizer heating rods, 4 regenerative heat exchangers and 1 moderator pump, has shown that initial dose rates of 10 ... 50 rad/h can be reduced down to 30 ... 300 mrad/h.

Satisfactory technical application of the MOPAC process involves the use of a mobile installation like the AMDA plant (Automatische Mobile Dekont-Anlage) developed by KWU; thus the decontamination work does not interfere with nuclear power plant installations. As an example using the mobile AMDA plant, 3 main coolant pumps of a PWR were decontaminated within 10 days involving radiation exposure to the 9 individuals concerned of merely 630 mrem, due to the extensive automation of the device.

The MOPAC process is not appropriate for the decontamination of systems or circuits with larger volumes because of the comparatively high salt concentrations of the solutions used. In these cases processes requiring lower concentrations of chemicals are needed, such as the CAN-DECON process developed by Atomic Energy of Canada, Ltd. (AECL), the Citrox-process of Pacific Nuclear, or the OZOX process of KWU. The decontamination of the steam generator channel heads of the American PWR Millstone-2 can be taken as an example of the OZOX application; during this work approximately 100 Ci were removed from the system resulting in an average DF of 7 [3]. Of course, such a decontamination requires large and expensive equipment, as can be seen in Fig. 2, where the Millstone set-up is shown schematically.

The lower DF obtained by the OZOX process, as compared to the MOPAC process is a direct consequence of using more dilute solutions while maintaining the principal chemical composition. In the OZOX process this disadvantage can be compensated by a modified preoxidation step resulting in DFs between 50 and 100 using very low reagent concentrations, as laboratory tests have demonstrated.

Where the BWR contamination layers consist of rather pure Fe_2O_3 a preoxidation step cannot succeed, of course. Therefore, a reducing pretreatment is chosen. This is done in the LOMI process (Low Oxidation-State Metal Ions) developed by the Central Electricity Generating Board, United Kingdom (CEGB) [4], by treatment with a V^{2+}solution which, in the presence of picolinic acid, exhibits a redox potential sufficiently negative to reduce Fe_2O_3. Moreover, this one-electron reaction is fast enough for technical application. Because of possible air oxidation of V^{2+} solutions, preparation of the reagent and also the decontamination process must be carried out in an inert atmosphere (nitrogen).

Reduction by V^{2+} fails where contamination layers include higher amounts of Cr(III). In these cases a preoxidation step using acid or alkaline permanganate solution (NP i.e. nitric permanganate or AP, alkaline permanganate) has to be applied. For economic and technical reasons, however, a direct application of one of the oxidizing processes mentioned above (e.g. OZOX) might be considered instead of LOMI.

The LOMI process was originally developed for the purification of fuel elements of the British Steam-Generating Heavy Water Reactor. Later LOMI, including a preoxidation step, was applied successfully to BWR recirculation line decontamination, where DFs of the order of 10 were obtained.

3.3. Electrochemical procedures

To complement or to provide an alternative to chemical procedures, electrochemical procedures have gained increasing importance during the past few years. The first reaction step involves anodic oxidation of the Fe(II) in the Fe_3O_4 compound. This is followed by a surface dissolution of the base metal starting from the active centers formed in the first step. In all these electrochemical procedures the anode is the base metal to be decontaminated. As a result of this mechanism, the contaminating layers are removed partly by dissolution, to the other part as non-dissolved oxides. The surface dissolution also results in polishing the metal surface, thereby removing contamination located in small cavities, etc., an effect very difficult to obtain by chemical procedures. Normally, electrolytes on phosphoric acid basis are used; as well as a smooth removal they also show good compatibility with the base metals under consideration.

An important prerequisite for the smooth removal desired, with the minimum electrolyte consumption, is application of optimum design of the installations, especially cathode geometry and electrolyte supply. Primarily, different designs are possible, and two of them, namely bath and sponge technique, are shown schematically in Fig. 3.

Using the bath technique, the specimen to be decontaminated is connected to the anode of the power supply and submerged in an electrolyte bath with a volume of up to several m^3. While the sidewalls of the vessel are normally used as a cathode, very often specially designed cathodes are inserted into the electrolyte bath.

In the sponge technique an acid-resistant sponge impregnated with electrolyte is inserted between the moveable cathode and the material to be decontaminated. During the decontamination procedure the sponge is moved across the surface. As an example of the sponge technique, decontamination of the main coolant pipes of the Obrigheim nuclear power plant should be mentioned; this has been done in connection with the steam generator exchange [5]. For this project a device carrying both electrodes and the electrolyte supply was designed and constructed to insert into the piping and to be remotely controlled.

Also special constructions can be used where necessary, e.g., for decontamination of the inner surfaces of steam generator heat tubes in the region of the upper U bend. In this case electrodes and electrolyte supply had to be moved inside the tubes (20 mm diameter), crossing distances up to 16 m and passing the whole U bend region. For economic reasons, due to the large number of heat tubes to be decontaminated (about 4000 in one steam generator), a device was designed for simultaneous decontamination of 10 tubes. This device is fixed to the lower side of the tube sheet by a socalled "finger walker" and can be moved to the next series of tubes by remote control. Tests using this device both in the laboratory and in the steam generator of a nuclear power plant have proved its technical suitability for such decontamination work.

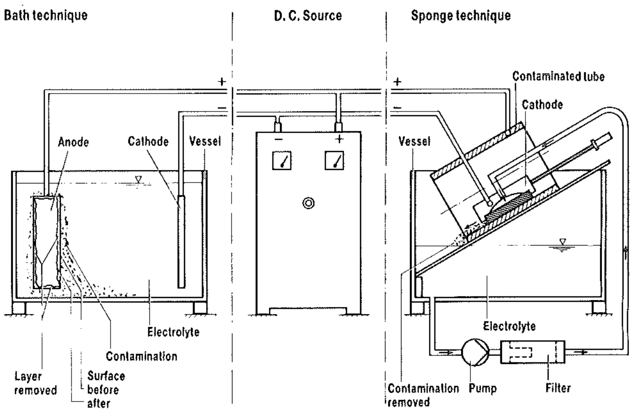

Fig. 3: Electrochemical decontamination; bath- and sponge-techniques (schematic)

Although electrochemical decontamination very often requires comparatively expensive installations, the technique is very attractive, because, using rather small volumes of electrolyte, DFs up to 100 can be obtained. Thus, as a pretreatment prior to repair work local dose rates can be markedly decreased.

4. Quality assurance

For decontamination techniques with practical applications, such as those mentioned above, these should be previously checked by detailed laboratory investigations, both with regard to DFs attainable and to compatibility with the base material.

Within a given procedure the DF depends on the solubility of the contamination layers, which, in turn, is governed by stoichiometry and morphology of the oxides present. Because of the strong influence of operational history on the properties a reliable determination of decontamination effectiveness is only possible using laboratory tests on representative samples. That means handling of radioactive materials and availability of controlled-area laboratories with appropriate equipment. Another important prerequisite is the availability of a pool of original specimens from different nuclear power plants, so that varying operational influences can be considered. If these conditions are not fulfilled in laboratory tests, experience has shown that disappointing results may be obtained on technical application.

The second item mentioned above, i.e. guarantee of compatibility of the technique with the materials under consideration, also requires extensive initial tests. Not only has direct damage to be positively excluded but there must be no harmful consequences arising during the years of continued plant operation after decontamination. Therefore, the necessary initial tests are not limited to the different materials present in the system, but they also have to consider different states of the materials, e.g. welding zones, sensibilization during operation and presence of stresses. From this it follows that detailed knowledge of materials technology is very important in the development and application of a good decontamination process.

For the examination of materials compatibility a stepwise sequence has been generally approved:

- pretreatment of the specimen under realistic conditions, i.e. generally autoclaving for approximately 6 weeks;
- multiple cyclic application of the decontamination process;
- further treatment under typical conditions for nuclear power plants for another 6 weeks;

- detailed examination of the specimen, e.g., by microscopy, metallography, scanning electron microscopy, corrosion testing.

These examples demonstrate that proving a decontamination process requires considerable expense. Only by these means it can be assured that the proper objective of decontamination will be reached, i.e. effective removal of contamination without producing any harmful effects on the integrity of the materials.

5. Conclusions

Due to limited space several important questions, such as

- recontamination,
- problems of decontamination below regulatory limits for unrestricted use and
- treatment of radioactive decontamination wastes

have not been discussed in this paper. Nonetheless, we believe that the short overview presented here gives an impression of the variety and number of modern decontamination techniques and of the actual state of their application to light-water reactors. On the other hand, the examples given illustrate that there is no single process for all applications and that it is not possible to have such a general process. Rather, it is necessary to select from a variety of possible processes the one which is best suited for the particular problem and, if necessary, to modifiy it. Quality assurance of the process is also of special importance.

Therefore, relevant experience is a prerequisite for successful development and application of a decontamination process. This means a close cooperation of chemists, materials specialists, process and design engineers and also the availability of well-equipped laboratories and workshops. It is also very important in preparing for a decontamination job to have a good liaison with the plant operators including detailed discussions in order to ensure that work runs smoothly and to give them and their experts confidence in the successful working of the decontamination process.

Without doubt all these measures require considerable expense, but they provide the only way to reach the objective of minimization of radiation exposure in an optimum manner.

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A new concept for product refining in the Purex process[1]

By E. Henrich, U. Bauder*, R. Marquardt*, W. G. Druckenbrodt** and K. Wittmann***

Abstract

In actual Purex plants the products are refined in additional solvent extraction cycles. Crystallization of uranyl and plutonyl nitrate from aqueous nitric acid solution is proposed as a potentially simpler product refining concept. Suitable crystallization conditions are being investigated in the laboratory using simulated and actual process solutions. A thorough removal of mother liquor is an essential purification step and well washed crystals usually contain less than one percent of an individual impurity. Crystallization simultaneously comprises a product concentration step. Hexavalent uranium can be separated from lower-valent plutonium. An outline of an integrated processing concept is given. Product refining by crystallization is compact; recycling of mother liquor plus wash acid prevents product loss and the generation of additional waste streams.

Zusammenfassung

Ein neues Konzept für die Produktfeinreinigung im Purex-Prozeß

Die Produktfeinreinigung in den heutigen Purex-Anlagen erfolgt vor allem durch Lösungsmittelextraktion. Kristallisation von Uranyl- und Plutonylnitrat aus salpetersaurer Lösung wird als potentiell einfacheres Feinreinigungsverfahren vorgeschlagen. Geeignete Kristallisationsbedingungen werden im Laboratorium an simulierten und realen Prozeßlösungen untersucht. Eine gründliche Entfernung der Mutterlauge ist der wesentliche Reinigungsschritt; gut gewaschene Kristalle enthalten normalerweise weniger als ein Prozent der Verunreinigungen. Die Kristallisation ist gleichzeitig ein Konzentrierungsschritt für die Produkte. Sechswertiges Uran kann durch Kristallisation von Plutonium niedrigerer Wertigkeit getrennt werden. Die Einpassung der Kristallisation in den Purex-Prozeß wird skizziert. Eine Produktfeinreinigung durch Kristallisation ist kompakt; Produktverluste und zusätzliche Abfallströme werden durch Rückführen von Mutterlaugen und Waschsäuren vermieden.

1. Introduction

The purpose of reprocessing spent nuclear fuel is to recover high purity plutonium and uranium with high yield. High purity products make fuel refabrication easier.

Previous and present objectives and priorities for processing spent nuclear fuels have changed from recovery of defense plutonium from low-burnup and short-cooled metal fuel to plutonium plus uranium recovery from high-burnup and long-cooled oxide fuel for reuse in power reactors. A multiplicity of alternative reprocessing techniques [1] were developed to different levels, mainly in conjunction with various reactor and fuel types. Some of the processes listed in Table 1 give an idea of the creative effort involved. Extensive accumulated experience provides the ground work for further development [2-4].

Safety and economy are priorities in all sections of a commercial nuclear fuel cycle. The Purex process has emerged worldwide as the chosen reprocessing technique [5]. Large-scale Purex plants began hot operation about 30 years ago [6], and most of the development work in the last two decades has been addressed to modifications and improvements of this process.

Though nuclear fuel reprocessing has much in common with processing of other highly toxic materials, consideration of radiation effects and prevention of criticality are additional unique characteristics. Radiation requires remote operation behind heavy shielding walls. Simple equipment and simple operations ease any additional remote preventive and corrective maintenance and help to maintain a high plant availability. Organic materials are usually more sensitive to radiation than inorganic ones. Prevention of criticality imposes constraints on equipment design and operating conditions. Therefore, reprocessing plants are among the most sophisticated and expensive chemical facilities. In this paper final product purification procedures in the Purex process are compared to a new and potentially simpler refining concept. In section 2, separation principles and possibilities for simplifying the product refining steps in the actual Purex process are discussed. In section 3, product refining by nitrate crystallization and its integration into the Purex concept are described.

2. Product recovery in the Purex process

2.1. Separation Principles

The most frequently used principle in chemical separation is selective distribution of individual components between two immiscible phases. The actual phase separation is the final step. Theoretically, there are only 5 combinations: solid/solid, solid/liquid, solid/gas, liquid/liquid, liquid/gas.

Operation is easier if at least one phase is a liquid or a gas. Except for a few volatile nuclides, the major separation steps in the aqueous Purex process occur at low operating temperatures and do not involve a gas phase; only solid/liquid and liquid/liquid separations are used in practice.

Additional phase separations may be generated directly from the initial mixture of species by changing the state conditions of one species, e.g., by distillation. Improved selectivity and ease of phase generation or separation may be obtained by conversion of the initial feed material into another set of species using auxiliary chemicals. One or more auxiliary phases, frequently liquid solvents, can simplify phase separation and accelerate reaction rates especially of solids. Chemical and phase function of auxiliary materials are frequently combined in practice, with one function being predominant. Auxiliary materials can be regenerated for reuse: the purification of

Table 1: Names of processes used in nuclear fuel reprocessing. State of development: C commercial use, P pilot plant, L laboratory studies

Aqueous processes:		
Solvent extraction		**Others**
C Purex	C Butex	P $BiPO_4$ precipitation
P Redox	L Amine	P Ion exchange
Non-aqueous processes:		
Pyrophysical		**Pyrochemical**
P Fluoride volatility	L Airox	P Melt refining
L Salt transport	L Fused salt-liquid metal	P Salt cycle
L Pyrozinc	L Tin nitride	L Molten salt electrolysis

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[1] Revised from a paper presented at the winter seminar on new developments in the field of reprocessing, Obertraun, Austria, March 4-10, 1984, organized by the Institut für Heiße Chemie, Kernforschungszentrum Karlsruhe, in collaboration with Gesellschaft Deutscher Chemiker and Gesellschaft Österreichischer Chemiker.

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auxiliary phases is generally less complex than a reconversion using auxiliary chemicals.

In the Purex process two immiscible liquid auxiliary phases, which also have some chemical function, are used: an aqueous nitric acid solution and an organic tributylphosphate (TBP) solution in dodecane. Liquids can be handled easily and reliably in many different operations. Two immiscible liquid phases allow the use of multistage counter-current contact in relatively simple equipment, to improve separation efficiency. These are major reasons for the preference of solvent extraction processes for spent nuclear fuel reprocessing.

High-purity and high-yield requirements generally cannot be satisfied simultaneously in a single separation step. Combination of two different steps, as shown in Fig. 1, is a usual processing mode: one step is designed to achieve high yield at the expense of purity (Y-step) and the other step is designed to achieve high purity at the expense of yield (P-step). A sufficiently reasonable yield in the P-step helps to maintain the recycling of impure product and plant throughput at a desirable low level.

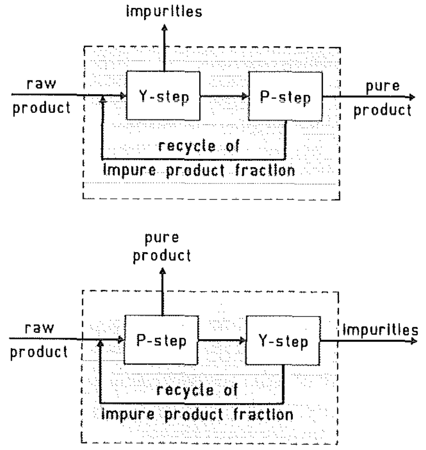

Fig. 1: Separation principle of product recovery in high yield and high purity

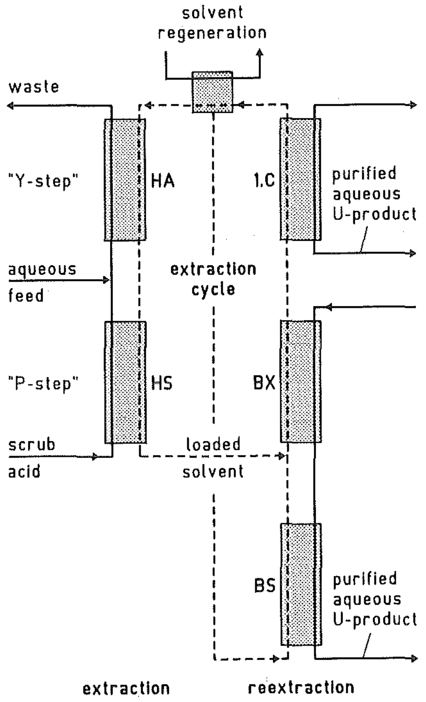

Fig. 2: An extraction cycle in the Purex process

A Purex extraction cycle as shown in Fig. 2 combines a Y- and a P-type separation. Extraction in the HA extractor corresponds to the Y-step and scrubbing in the HS extractor to the P-step. The aqueous stream from the HS to the HA extractor recycles some impure product. The organic product stream usually contains less than 0,1 % of most waste nuclides. Primarily due to the somewhat poorer separation selectivity of the TBP extraction system for Zr, Ru, Tc and Np [7], product purity is still insufficient for direct fuel refabrication. Therefore, the products have to be reextracted and the extraction repeated once or twice under slightly modified conditions.

2.2. *Conclusions and corollaries*

Actual Purex concepts comprise up to 5 extraction cycles, e. g., a highly active U/Pu separation cycle plus 2 additional purification cycles for each product. Practical experience has shown that the integral purification efficiency decreases in successive extraction cycles. This is frequently observed in multicomponent systems and provides an incentive to apply an alternative separation principle.

Compared to the fuel components, the volumes of auxiliary phases in a Purex plant are relatively large. In a 5-cycle process about 40 m^3 of organic solvent and about 15 m^3 aqueous phase are contacted with 1 Mg of fuel. Regeneration and recycling of the unloaded auxiliary phases is a major element of waste volume minimization. The aqueous phase is purified by distillation and reused several times and the organic solvent is purified by a soda wash and reused more than 100 times. Details of an efficient phase regeneration are somewhat more complex. The aqueous and organic phases are not completely unaffected by each other. Attention must be paid to the mutual solubility of components and to phase entrainment as well as to the chemical and radiolytic solvent degradation products.

After a first extraction cycle, the residual fission products (FPs) amount to only about 100 ppm of the products. The large solvent volumes in the subsequent cycles are required to selectively dissolve the massive 99.99 % fraction of product nitrates. Considerably smaller amounts of auxiliary materials would be required to selectively affect the properties of the small impurity fraction. A product refining concept using no or only moderate amounts of a second auxiliary material would be desirable.

3. Product refining by nitrate crystallization

3.1. *Selection of a suitable product refining principle*

Suitable alternative product refining concepts for the Purex process are confined to the aqueous U- and Pu-nitrate solutions from a first extraction cycle. Solvent extraction or precipitation of the small amount of impurities is an option but not a simple task, due to the many different chemical species involved. Another straightforward option, which also does not require large amounts of auxiliary materials, is crystallization of uranyl- and plutonyl-nitrates (UNH and PUN) by evaporation and cooling of the nitrate solutions. Moreover, crytallization combines a product purification with a product concentration step. This new product refining principle is now being studied using simulated and actual process solutions.

Purification and concentration of dissolved solids by crystallization on cooling or evaporation is a well-established, conventional and efficient procedure. The technology is known from many industrial applications. The strict geometry of a crystal lattice is the basis of the high purification efficiency. Crystalli-

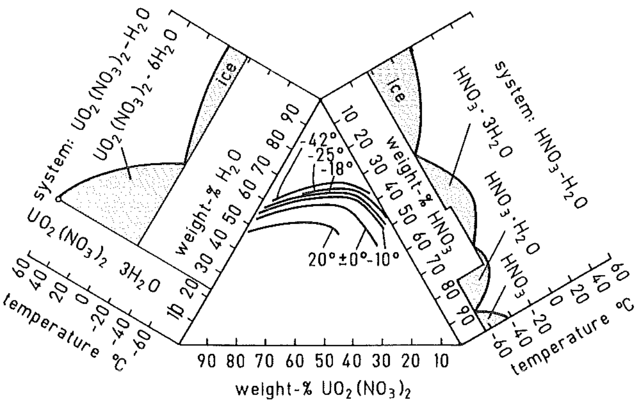

Fig. 3: Phase diagram of $UO_2(NO_3)_2$ - HNO_3 - H_2O

zation is very well known and has been used for many centuries to prepare pure materials. Even chemically very similar compounds have been separated in this way. The shape of anions and cations in the crystal lattice of uranyl- and plutonylnitrate deserves special notice: The NO_3^- anion is planar, whereas the UO_2^{2+} and PuO_2^{2+} cations are linear. Such anion and especially cation shapes do not occur frequently. Isomorphous replacement by similar ions is therefore unlikely even from the multitude of FP species in fuel solutions [8, 9].

3.2. Basis of uranyl and plutonyl nitrate crystallization

A sufficiently high crystallization yield of U(VI) and Pu(VI) nitrates can be obtained at high feed concentrations and low solubilities at the end of the crystallization process. The solubility of UNH depends on temperature and nitric acid concentration as shown in Fig. 3 [8, 10, 11]. A range of low solubility extends from 6 to 12 M HNO_3 at temperatures between – 42 and – 18 °C. Actual procedures and suitable crystallization conditions can be taken from the following example: A 1.4 M UNH-solution in about 6 M HNO_3 is agitated and cooled down from 30 to about – 30 °C in the course of 0.5 to 1 h. In the mixed suspension the UNH crystals grow to a size of 0.1 to 0.3 mm.

Sedimentation of the crystals is fast due to their size and density. The volume of the settled crystal cake is about 40 % and the volume of the true crystals about 25 % of the feed volume. Impurities and free HNO_3 remain in the mother liquor; the HNO_3 is concentrated close to 8 M HNO_3. A crystallization yield of 95 % can be achieved, since the residual U(VI) concentration is only about 0.07 mol/l. Still higher yields are possible at higher feed concentrations. At feed concentrations above 2 mol/l UNH the crystal suspension density becomes inconveniently high.

Suitable operating conditions for PUN crystallization are comparable to those for UNH. Preliminary results indicate a slightly lower optimum HNO_3 concentration in the mother liquor. Nitrates of Pu(III or Pu(IV) are less stable or more soluble and not well suited for crystallization. They must be oxidized to Pu(VI) prior to crystallization. A suitable oxidation procedure is part of the AUPUC process for fuel refabrication [12].

3.3. Laboratory studies

Simulated solutions were prepared by dissolving UNH in 6 ... 10 M HNO_3. The 1 ... 2 M UNH solutions were spiked with various amounts of either individual radionuclides or small volumes of fuel dissolver solution or highly or medium active waste solutions. The FP element concentration range corresponded to a second or a third extraction cycle. In addition, two active process solutions were obtained from a breeder spent fuel reprocessing campaign in the MILLI plant: an aqueous U-product solution from the first extraction cycle and an aqueous Pu-product solution from the second extraction cycle. Both solutions could be handled in a glove box without much additional shielding.

Crystallization feed adjustment was made as follows: concentration by evaporation to about 2 mol/l heavy metal, oxidation to Pu(VI) in the case of Pu, adjustment of heavy metal and HNO_3 concentrations by addition of HNO_3 solution. Usually, 0.1 l batches of a UNH feed solution were transferred into cylindrical crystallization vessels, equipped with a cooling jacket and a glas frit at the lower end. Either a stirrer or air bubbling through the glas frit maintained nearly homogeneous crystallite suspension during cooling from slightly above room temperature down to about – 30 °C in the course of 0.5 to 1 h. Then agitation was discontinued; the crystal cake settled in less than a minute and the mother liquor was drained off. The remainder of the mother liquor adhering to the crystals and vessel walls was washed off once or several times, using small batches of cold nitric acid at about the temperature and concentration of the mother liquor.

The amount of product and waste nuclides were determined in aliquots of the feed, mother liquor, wash acids and the washed crystals by conventional methods, gross α-, β- and γ-counting and by routine γ-spectrometry using a Ge(Li) detector. The most important decontamination step involves thorough removal of adhering mother liquor from the wet crystals. Gross γ-decontamination factors (DFs) in successive washing steps are shown in Table 2. Temperature and HNO_3 concentration of the wash acid corresponded to the mother liquor. Wash acid batches amounting to 10 % of the feed volume were mixed with the wet crystal cake and the surplus was removed from the settled crystals. The stepwise increase of the DF indicates that 8 ... 9 % of the mother liquor adhers to the crystals and less than 1 % of the impurities is contained within the crystal lattice.

The individual DFs of representative FPs and transuranics (TUs) in Table 3 were determined by routine γ- and α-spectroscopy. In the purified product most FPs were below our detection limit. The feed termed 1CU was an adjusted U-product stream from the first extraction cycle of a fast reactor spent fuel reprocessing campaign. To simulate the activity level of a subsequent extraction cycle, the 1CU feed was diluted with UNH-solution by a factor of 100 and designated "1CU spiked". Two crystallization cycles were carried out and the wet crystals were washed only once. Except Pu, the different

Table 2: Gross gamma decontamination factors in successive washing steps. Feed: 1 M $UO_2(NO_3)_2$, 5.7 M HNO_3, HAW or MAW spike; cooling from room temperature to – 26 °C in 0.7 h

spike	number of washing steps			
	0	1	2	3
HAW	12	32	71	131
MAW	11	25	61	130

Table 3: Decontamination factors of individual nuclides. Feed: 1 M $UO_2(NO_3)_2$, (6.2 ± 0.2) M HNO_3; two successive crystallization cycles; > below detection limit

Sample	Ru-106	Cs-137	Am-241	Pu
ICU	319	> 100	272	286
ICU spiked	253	> 140	253	23

impurity concentration level does not affect the DFs appreciably. The lower DF of Pu in the spiked solution is attributed to the presence of some Pu(VI). Other experiments proved that cocrystallization of Pu and Np can be supressed by reducing conditions: in the presence of very small U(IV) fractions, the lower-valent Np and Pu species remain in the mother liquor. A separation of U and Pu is possible in this way. The products are pure UNH and an impure Pu(IV)/U(VI) "master blend". The blend can be purified after oxidation of Pu(IV) to Pu(VI). All FPs checked to date including Ru, Zr and Tc as well as Fe, Cr and Ni corrosion products were removed with the mother liquor. Under suitable crystallization and washing conditions, usually less than 1 % of an individual impurity were contained within the crystal lattice. For some couples of FPs, slightly different DFs were observed. Fine suspensions of solids in slightly turbid feed solutions are also removed, especially if the mother liquor is removed by decantation.

Hexavalent Np accompanies the Pu(VI) during PUN crystallization and can be burned in fast reactors.

3.4. Outline of an integrated processing concept

In the product streams from a single highly active Purex separation cycle the FP nitrates are far below their solubility limits. The solutions must be concentrated by evaporation and adjusted to the desired concentrations of at least 1,4 mol/l heavy metal and 5 ... 6 mol/l HNO_3 for crystallization. Slightly reducing conditions should be maintained in the course of UNH crystallization to remove TU elements. Careful Pu(IV) concentration, to prevent formation of polymers, plus an additional oxidation step from Pu(IV) to Pu(VI) is required prior to PUN crystallization.

Another option is a reversed sequence of oxidation and concentration steps.

Nitrate crystallization plus washing cycles can be repeated until the product specifications are attained. Mother liquors and wash acids are combined and a pure nitric acid for reuse in subsequent crystallization cycles can be recovered by distillation. The small product fraction plus traces of waste nuclides are concentrated in the evaporator sump and are recycled to the extraction feed as shown in Fig. 4.

Assuming a retention of 3 or 1 % of an individual impurity in the washed crystals, a total DF above 10^3 can be achieved with two crystallization cycles. A heavy metal concentration of 1.4 mol/l or more in the crystallization feed and a volume of wash acid comparable to the crystal volume should result in a single crystallization yield of more than 93 % and less than 14 % product recycle for two crystallizations in succession. The extraction cycle throughput will be increased by less than 15 % correspondingly. UNH and PUN recovery by crystallization from separate evaporator sump solutions plus recycle to the corresponding crystallization feed is an option to reduce extraction feed recycling to a few percent.

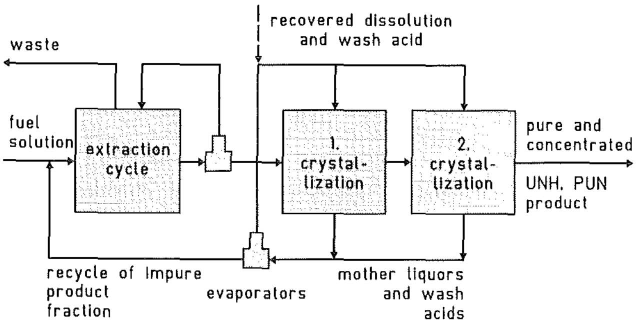

Fig. 4: Outline of a one-cycle Purex process plus product refining by nitrate crystallization

Using the above assumptions and a crystallization cycle time of 1 h, the total solution volume in 2 crystallizers, operating in parallel, amounts to only about 0.3 m^3 for a 1 Mg heavy metal per day plant. Evaporation and refrigeration energy requirements even without heat exchange are only about 0.3 and 0.03 MW respectively. The prior concentration of product streams from the extraction cycle requires about three times as much energy.

A convenient and process compatible refrigeration energy transfer fluid is 33 % HNO_3 (melting point − 42 °C.

3.5. Characteristics of product refining by extraction and crystallization

Major advantages of product refining in the Purex process are the ease of counter-current multistage operation, the high yield and separation efficiency of a TBP extraction cycle, the availability of reliable extraction equipment and, especially, the high state of development obtained from commercial experience. Less favourable characteristics are connected with the rather large volumes of organic solvent. The solvent must be stored and regenerated to remove chemical and radiolytic degradation products. A solvent fire must be prevented. Regeneration of aqueous phases, concentration of aqueous product solutions, and recycle of process streams containing traces of products and waste nuclides can be complicated by the presence of organic impurities.

The most obvious disadvantage of product refining by nitrate crystallization is the considerably lower state of development. This includes some risk that presently unknown details may jeopardize the concept. But the potential technical and safety advantages, summarized below, are an incentive and a justification to continue investigation:

More compact processing. Processing more concentrated aqueous solutions and avoiding large solvent volumes results in less operations, less equipment and cell space requirements. The final product concentration steps are integrated.

No waste streams and no product loss. Complete recycling of a small product fraction plus traces of waste nuclides serves to prevent product loss and saves subsequent waste management steps.

Conventional equipment and operating conditions. Cooled and agitated crystallization vessels are simple equipment. Operating conditions are easily controlled. Inventories are relatively low, steady state conditions are attained in a short time and frequent start-up and shut-down do not cause problems.

Partial substitution of fuel refabrication headend. Products are directly compatible with the AUPUC process or microwave denitration or fuel refabrication.

4. Conclusions

Product pruification and concentration by crystallization of uranyl and plutonyl nitrates from nitric acid solutions at low temperatures shows promise for simplifying the product refining steps in the Purex process. The investigations are therefore continuing and the major aims comprise.

- more detailed information on the behaviour of various FPs and other impurities at different concentration levels, use of inactive carriers;
- optimization of the crystallization procedure in view of cooling rates, feed concentrations, agitation, etc.;
- development of improved crystallization equipment;
- minimizing the wash acid volumes at high washing efficiency;

- improvements in oxidation and concentration procedures for Pu(IV) solutions;
- design of crystallization flowsheet options.

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