

FISSION MOLYBDENUM FOR MEDICAL USE

PROCEEDINGS OF A TECHNICAL COMMITTEE MEETING
ORGANIZED BY THE
INTERNATIONAL ATOMIC ENERGY AGENCY
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FOREWORD

Because of its favourable physical and chemical properties, ^{99m}Tc is today the radionuclide of choice for routine diagnostic nuclear medicine. The parent radionuclide ^{99}Mo is produced mainly by the nuclear fission of ^{235}U . Small amounts are produced by the neutron activation method, however, current generator technologies are not yet fully developed to utilize the so-called " n, γ ^{99}Mo " in medium or large production scale.

There are several countries, particularly those with sizable local demand, seriously considering the possibility to locally produce ^{99}Mo through the fission route. In view that the required technology is highly sophisticated and that the necessary capital investment is very high, some Member States have requested the co-operation of the Agency for technical advice.

In response to the growing interest in this matter, and in order to provide some guidelines both to the Agency and to interested Member States, the IAEA convened the Technical Committee Meeting on "Fission Molybdenum for Medical Use". The report includes an assessment of the current target and process technologies, problems associated with radioactive waste disposal as well as views on economical factors and proliferation concerns. Also included are all the contributions presented at the meeting by individual participating countries.

The Agency wishes to thank all the scientists and institutions who contributed to the meeting with their ideas and scientific papers.

The officer of the IAEA responsible for the meeting was H. Vera Ruiz of the Division of Physical and Chemical Sciences.

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SUMMARY REPORT

1. INTRODUCTION

Technetium-99m is today the most widely used radionuclide in modern diagnostic nuclear medicine; very likely this will remain so for the foreseeable future. This is mainly because of its favourable nuclear properties and the fact that it was possible to produce compact, practical and transportable ^{99m}Tc - ^{99}Mo generator systems, providing significant amounts of ^{99m}Tc to users far removed from the production centres.

The ever increasing demand for this radionuclide, both in developed and developing countries, may call for a greater production capacity and availability, particularly in the developing countries, many of which currently operate low and medium power nuclear research reactors.

Currently, the nuclear fission of ^{235}U is the preferred method of producing high specific activity ^{99}Mo suitable for the preparation of chromatographic generators. The drawback of the fission ^{99}Mo technology, at least from the view-point of a developing country, is the high capital investment and the relatively sophisticated technology required. In spite of the above, there are several countries with sizeable nuclear medicine communities seriously considering the possibility of introducing this technology to reliably meet the local demand of ^{99m}Tc .

Most of the present fission ^{99}Mo technologies make use of highly enriched ^{235}U (HEU) as Al-U alloys or UO_2 in a variety of target designs, and the corresponding chemical separation processes have been developed accordingly. However, there are indications that the availability of HEU targets may be restricted in the future and that new or modified target technologies and separation methods have to be investigated to ensure a high quality and economical $^{99}\text{Mo}/^{99m}\text{Tc}$ product when using low enriched target materials (LEU).

2. SCOPE OF THE MEETING

Countries wishing to set up production plants for fission ^{99}Mo to meet ever increasing national demands of $^{99\text{m}}\text{Tc}$ for medical purposes, should seriously and timely take into account the desirability of using low enriched uranium in this process. In this regard, the Agency should continue to play an active role in facilitating an exchange of information and ultimately an appropriate transfer of technology between developed and developing Member States by organizing scientific meetings and through its Technical Co-operation Programme.

The meeting was held at the Nuclear Research Centre of Karlsruhe, Federal Republic of Germany, from 13 to 16 October 1987, and was attended by eleven specialists from 6 Member States. All papers presented at the meeting are included at the end of the report.

In particular, the participants were asked to:

- review the known current production technologies of fission ^{99}Mo for medical use including target technology, post irradiation chemical processing, waste disposal, recycling of target material and reactor irradiation practices;
- discuss and assess the feasibility of substituting low enriched uranium for highly enriched uranium in targets, particularly with regard to new target materials and technology (i.e. high density uranium-silicide dispersions and uranium metal films), purity of the ^{99}Mo product, radioactive waste and economics of the process;
- assess the feasibility of transferring this technology from developed to developing countries and identify possible bottle necks and problem areas that may hinder this technology transfer; and
- identify and define concrete future lines of activity where the Agency's efforts would have the greatest impact and significance.

3. TARGET TECHNOLOGY DEVELOPMENT

Most of the world's ^{99}Mo is produced from the following three target geometries:

- (1) UO_2 films on the inside walls of stainless steel cylinders,
- (2) Uranium-aluminide alloy extruded into aluminium clad rods, and
- (3) Uranium aluminium dispersed in an aluminium matrix and pressed between aluminium plates.

The first design is unique to ^{99}Mo production; the second and third designs are fabricated in the same manner as fuel for nuclear research and test reactors.

Conversion of present HEU ($\sim 93\%^{235}\text{U}$) targets to those using LEU ($\leq 20\%^{235}\text{U}$) requires a 5-6 fold increase in total uranium content to produce irradiation yields of ^{99}Mo equivalent to current HEU targets. The incorporation of this larger concentration of uranium in current target geometries will require modifications of the fuel composition. In the case of HEU-oxide-film targets, research at Argonne National Laboratory (ANL) has been directed to the development of LEU metal films which can directly replace the UO_2 films used in current target designs. It is possible to place uranium films on the inside wall of cylindrical targets by either loading uranium metal foils or electrodepositing uranium metal. The work at ANL has concentrated on development of the electrodeposition technique.

Uranium metal targets for fission ^{99}Mo production have several advantages over UO_2 targets. For example, uranium metal is about twice as dense as UO_2 , its thermal conductivity is an order of magnitude higher than that of UO_2 , and its plating efficiency from LiCl-KCl-UCl_3 molten salt melts is 100% vs. 20% for the UO_2 deposition process. The principal disadvantages of using electrodeposited uranium metal targets are that (1) they must be prepared from molten salt systems at high temperatures ($\sim 450^\circ\text{C}$) in an inert atmosphere, and (2) the deposit morphology tends to be dendritic. While the higher conductivity and density make uranium metal targets appear quite promising, heat management and safety issues need to be thoroughly analyzed.

Experiments performed on simulated LEU targets have shown that (1) well-bonded dendrite-free uranium metal films can be bonded to nickel-plated stainless steel or zircalory and (2) it is likely that LEU targets can be processed using the current techniques for HEU oxide targets, with no significant changes. Uranium metal can be easily dissolved and the higher amounts of uranium in the target will affect neither ^{99}Mo yield nor its purity. It is expected that the higher amounts of transuranic (TRU) elements produced by the irradiation of LEU will be handled easily by current processing steps.

The development of U_3Si_2 and U_3Si fuels has made core conversion from HEU to LEU possible in most research and test reactors currently using U-Al alloy or uranium aluminide fuels. For ^{99}Mo production targets containing HEU alloy or aluminide fuel, the use of replacement of targets containing LEU silicide fuel and the same target geometry would retain current irradiation yields of ^{99}Mo . Because these targets will be fabricated in the same manner as reactor fuels, their ability to be fabricated will be assured and difficulties in licensing will be minimized. However, because of (1) the different chemical forms of uranium (e.g., U_3Si_x vs UAl_x) and (2) the need for harder cladding (e.g., Al 6061, AlMg_2 or AG3NE aluminium alloys vs pure aluminium), modifications in the current commercial chemical processes for ^{99}Mo recovery will be necessary. Although it is clear that processes can be modified and/or developed for LEU silicide targets, there are, however, serious concerns that these developments will be extremely difficult to integrate into ongoing production facilities without disruption of production schedules.

The Chalk River Nuclear Laboratories (CRNL) has performed cold and hot testing of the ability of their current processing method to handle LEU silicide targets that were fabricated using materials and a geometry compatible with the fabrication method for LEU fuel rods. These tests have shown that the current process method cannot be used directly to process LEU silicide targets. Two problems were discovered:

- (1) A silicate precipitate from the acid dissolution of the targets was finely divided and difficult to filter, and plugged the alumina column during processing.

(2) This precipitate adsorbs Mo and holds it against elution from the column. (This problem was not evident in cold laboratory tests but was noticed in hot testing using an actual full-size target.)

Tests at ANL, using simulated targets, have shown that process modifications can be made to the alkaline dissolution process to contend with problems developed from the use of silicide fuels. Tests with slightly irradiated targets are planned in early 1988.

New target designs that will not require changes in current processing methods, have a great appeal, even though their fabrication is expected to be more expensive and licensing more difficult.

Some alternative target designs of this type have been addressed at CRNL. These designs include U metal, UO_2 , U-Al alloy, U dispersed in aluminium, UO_2 dispersed in aluminium, and other combinations. Because UO_2 is economically attractive due to ease of preparation, its use in an aluminium dispersion has been explored to the point of fabrication of full-size targets and cold laboratory testing. This target was fabricated by extruding a 3 m rod of UO_2 dispersed in aluminium at 60 wt % U. The extrusion required a large press and UO_2 was not uniformly dispersed throughout the rod. The rod was clad with pure aluminium. It was then cut into target lengths and processed in the laboratory by dissolving, adding tracer ^{99}Mo , and processed by an alumina column. Difficulties with fabrication of the UO_2/Al rod may be solvable. However, other target compositions continue to be explored, including those made separate from reactor fuel fabrication.

In conclusion, LEU targets for ^{99}Mo can be fabricated to give yields typically of current HEU targets. It is likely that changes in target design and/or processing will be necessary for this conversion. The economical impact of this conversion has to be assessed.

4. CURRENT PROCESS TECHNOLOGY

Six papers were presented on different process technologies of ^{99}Mo . R. Marqués (Argentina), A. Sameh (FRG) and C. Fallais (Belgium) reported on results of processes based on the irradiation of highly enriched (>90% U-235) targets in several High Flux Reactors ($\Phi > 10^{14} \text{ n/cm}^2 \text{ s}$) and alkaline dissolution of different U-Al targets. These processes differ mainly in the subsequent purifications steps of the crude ^{99}Mo . K.A. Burrill (Canada), R. Münze (GDR) and H. Kudo (Japan) described ^{99}Mo production processes that use acidic (HNO_3) dissolution. A slower rate of dissolution has been occasionally observed in the GDR and Canadian processes. Limited data indicate that this may be correlated with higher burn-up. During routine production, GDR personnel have experienced 20-50% lower yields because of the formation of a gelatinous precipitate arising from the presence of silicon in the cladding.

Whereas the Canadian process starts with highly enriched targets, the GDR process uses medium enriched U-Al-targets (fuel elements of the research reactor, 36% enriched). Kudo reported on a method based on 2.6% enriched UO_2 pellets. All of these processes include separation of ^{133}Xe . In some cases ^{131}I is separated as well.

All processes discussed during the meeting have been demonstrated to supply ^{99}Mo of a sufficiently high quality for preparing column generators for medical use.

5. PROBLEMS ASSOCIATED WITH WASTE DISPOSAL

Processing highly enriched targets for ^{99}Mo production generates radioactive wastes which must be treated and disposed of in environmentally acceptable ways.

The wastes will be generated as solids, liquids, and/or gases, and will include material in the low, medium, and high radioactive level classifications. Initial treatment of the wastes is usually required at the production site, prior to short or long term storage. The treatment required is dictated by both the form of the waste and its activity level. This technology is established, and generally available.

The heavily shielded process and interim storage facilities must obviously be built on-site, but the sophisticated equipment required for them would generally have to be bought off-shore.

Storage facilities may or may not need to be constructed, depending upon the physical and political availability of off-shore space.

In any event, an adequate infrastructure is required to transfer waste from the fuel processing facility to the waste treatment facility (if not one and the same), and the treated waste to storage.

Trained operating crews, and support personnel (maintenance, analytical, accounting, safety, security, etc) are required for all facilities. In addition, an independent regulatory body is required, to review, license, and monitor all phases of the operation.

6. ECONOMIC FACTORS

At present the world's supply of ^{99}Mo comes mainly from commercial sources. In Eastern Europe, the German Democratic Republic is the only known manufacturer with a capability of 1000 Ci/week. Medi-Physics (USA), IRE (Belgium) and AECL (Canada) are the other major suppliers in Western Europe and North America. IRE and AECL both have a capability of 3000-5000 Ci per batch. The number of batches per week can vary according to the demand. It is estimated that this installed capacity can supply current world's needs for ^{99}Mo on a reliable basis. KfK has demonstrated a capability of producing 1000 Ci ^{99}Mo per week on a routine basis, however, their mandate excludes them from commercial activities and their efforts are dedicated to research into process development.

Several companies, including the largest producers of $^{99\text{m}}\text{Tc}$ generators in industrialized countries, have chosen on economical grounds to manufacture $^{99\text{m}}\text{Tc}$ generators by purchasing fission ^{99}Mo rather than by producing it. In certain developing countries, however, there are more than simple economic factors that may drive the demand for ^{99}Mo fission production. Socio-economic factors, hard currency availability and a need for technological development provide some of the driving forces.

Before undertaking production of fission ^{99}Mo , a country must first have or develop an appropriate infrastructure. This includes a suitable reactor with a flux greater than 10^{13} n/cm².sec, an isotope processing facility with Health Physics, Regulatory Affairs, Quality Assurance and Quality Control organizations. In such a facility, appropriate hot cells each with sufficient shielding and glove boxes are estimated to be a minimum requirement. In addition there can be significant costs associated with technology transfer, training and start-up.

The country should also have adequate waste storage and management facilities. However, if these are on the same site as the processing facility and reactor, issues such as the acquisition of containers approved for road transportation and the costs associated with such transport might not be factors. These costs could be significant otherwise.

KfK has provided actual costs for a weekly production of ^{99}Mo . This includes chemicals, maintenance, waste disposal, transportation, irradiation services, health physics, quality control and production. It was stated to be DM 2.4 million annually. This did not take into account R&D costs. It is recognized that an individual country may choose not to allocate these R&D costs and overhead to the cost of ^{99}Mo production.

With DM 2.4 million (US\$1.3 million) one could buy ~ 130 Ci/week of ^{99}Mo for a period of one year (6 day Ci delivered) assuming a price of \$200/Ci which is appropriate for that large volume. This break-even point of 130 Ci/week will vary from country to country. At this level of demand, based on the KfK production costs, it seems reasonable that a country may consider making its own ^{99}Mo . There are considerations other than economics that can be important factors as stated earlier.

7. PROLIFERATION CONCERNS

7.1. Highly Enriched Uranium Contained in Fission ^{99}Mo Production Targets

Due to international concerns about the proliferation of weapons-useable uranium and because supplies of highly-enriched uranium (>20%) will be restricted in the future, a programme has begun at ANL to develop the technology for production of fission product molybdenum using targets containing low-enriched uranium (< 20%) instead of highly-enriched uranium. The status of this work is discussed in the paper entitled "Preliminary Investigations for Technology Assessment of $^{99\text{m}}\text{Mo}$ Production from LEU Targets".

7.2. Plutonium Produced in Fission ^{99}Mo Production

The plutonium produced in irradiated targets containing HEU (93%) or LEU (20%) for production of fission product molybdenum is not significant from a proliferation point of view.

Targets specifically designed for fission ^{99}Mo production contain between 1 and 15g ^{235}U . Burnup is typically 1-2% of the ^{235}U because the ^{99}Mo saturates in this burnup range. Quantities of plutonium produced are about 1 mg/1000 Ci ^{99}Mo for targets containing HEU and about 21 mg/1000 Ci ^{99}Mo for targets containing LEU. Curies are defined here at the time of removal from the reactor and the Pu includes both ^{239}Pu and ^{239}Np . With LEU targets, it would require production (at the reactor) of about 48,000 Ci ^{99}Mo to produce 1 g of Pu. That is, about 1g of Pu would be produced per year for a ^{99}Mo production rate of 1000 Ci per week. This rate of Pu production is not significant.

7.3. Uranium Recycling

Some concern was expressed about the possibility that the transfer of technology for uranium recovery from the ^{99}Mo fission production process may potentially lead to activities in sensitive areas such as reprocessing of irradiated fuel elements. It must, however, be recognized that such transfer would be limited to small scale operations aimed exclusively at the recovery of the valuable uranium from LEU as well as HEU targets. In both cases the production of Pu is negligible

and the underlying chemical process flowsheets are well described in the open literature. Further, it is recognized that the KfK process technology is not directly applicable to the recovery of fissionable materials other than uranium.

8. SAFEGUARDS

Safeguards requirements must be fulfilled by a very strict (at the mg level) ^{235}U and U total balance for each area and at all times.

Documented reports must be sent at regular periods to national and international authorities. Fission ^{99}Mo producers must accept regular inspections by national and international authorities, particularly by IAEA officers.

9. QUALITY ASSURANCE AND QUALITY CONTROL

For fission ^{99}Mo , a quality assurance programme must be completely described including:

- detailed description of the facility and equipment,
- detailed description of the whole process, such as targetry, irradiation, chemical process, storage, waste and recovery,
- personnel training,
- good manufacturing practices and good laboratory practices,
- technical procedures.

Final ^{99}Mo quality must be described by precise specifications of radionuclidic and radiochemical purities in addition to other requirements such as specific activity, pH and nature of solution as described in the international pharmacopoeia.

Final product quality must be assessed by a qualified quality assurance officer who is functionally independent from the production department and assumes personal responsibility for the assessment.

10. POSSIBILITIES FOR TECHNOLOGY TRANSFER

Efficient and reliable international suppliers of ^{99}Mo are in existence today, with estimated total capabilities sufficient to supply the entire current world demand. However, for a variety of reasons, some organizations in developing countries may wish to undertake indigenous production of fission ^{99}Mo for medical applications. The meeting considered and discussed several areas in which the IAEA may assist these organizations in achieving their goal through a process of technology transfer.

Nuclear Reactor Requirements

Before embarking in ^{99}Mo fission production, the organization should make sure that adequate irradiation facilities are available. These facilities should include a nuclear research reactor with the following characteristics: (a) Irradiation positions with adequate thermal neutron flux greater than $10^{13} \text{ n/cm}^2 \cdot \text{sec}$ must be available^{*/}. The ability to insert and remove targets without interrupting reactor operation is desirable but not necessary, (b) The coolant flow in the irradiation positions must allow irradiation of the fission targets with acceptable thermal-hydraulic safety margins. (c) Operation of the reactor must be reliable and continuous, with sufficiently high load factors, (d) Other uses of the reactor are desirable to reduce the fraction of the operation costs to be allocated to ^{99}Mo production.

Safety Considerations/Regulatory Aspects

Irradiation of the targets is normally regulated by the same organization which has regulatory responsibility for the operation of the reactor. In all probability, the same criteria applied to evaluate the safety of the reactor fuel will be used to evaluate the safety of the targets. Thus, thermalhydraulics considerations will dictate the maximum power of the targets, their uranium content, and the uniformity requirements for their loading. The safety aspects of the fissile

^{*/} Experience shows that to obtain a ^{99}Mo activity of about 150 Ci at a calibration time of 6 days after the end of irradiation, a thermal neutron flux of 3 to 4 x $10^{13} \text{ n/cm}^2 \text{ sec}$ is required.

material used in the targets will also be evaluated in a manner consistent with the evaluation of the reactor fuel. Thus, targets using the same material as the reactor fuel material will be easiest to license.

The safety aspects of target processing must be addressed in a separate safety report, which must include a detailed quality assurance programme (see Chapter 9 on quality assurance programme).

Waste Disposal

An adequate waste disposal/uranium recovery system must be available before start-up of the facility (see Chapter 5 on waste disposal).

Man-power Requirements

An infrastructure of skilled personnel in nuclear, chemical and radiochemical fields must be available.

Availability of Fuel

HEU supplies may be limited in the future. Organizations in developed countries are investigating the feasibility of using LEU targets in their facilities. Organizations in developing countries should take this development into account (see Chapter 7 on Proliferation Concerns).

Economical Aspects

The demand for ^{99}Mo which the proposed facility is planned to satisfy must be assessed realistically in terms of quantity of ^{99}Mo needed per week in the various nuclear medicine centres of the country. The level of demand is essential to determine the unit cost of the produced ^{99}Mo . A realistic estimation of the unit cost should take into account several factors such as R & D costs, capital investment of the production plant, operation costs, quality control and maintenance of all the relevant facilities. The assessment can be done by conducting a technical-economical feasibility study.

11. SUMMARY OF CONCLUSIONS AND RECOMMENDATIONS

1. Since the establishment of indigenous production facilities of fission ⁹⁹Mo for medical use requires serious considerations of technical and economical nature, it is highly recommended that careful pre-feasibility and feasibility studies be conducted before further commitments are made. The Agency may play a role, in co-operation with external experts, to help the country concerned to define the terms of reference for such feasibility studies.
2. It is recognized that safety and regulatory aspects are of paramount importance for a successful production programme. Therefore, it is recommended that both national and international safety regulations should be strictly followed.
3. Because of the technical complexity of the matter, it is necessary that the staff involved in all phases of the production programme be well trained and highly qualified. Here again, the Agency may play an important role through its Fellowship Programme.
4. It is expected that in about two more years new developments in target materials and technology as well as chemical processing may take place, which will take into account the future unavailability of highly enriched uranium for targets.

PAPERS PRESENTED AT THE MEETING

OPERATION OF THE INSTALLATION FOR FISSION ^{99}Mo PRODUCTION IN ARGENTINA

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Abstract

The paper describes the efforts of the Argentine Atomic Energy Commission to establish a programme to produce fission ^{99}Mo for the preparation of $^{99\text{m}}\text{Tc}$ generators. The production plant has been completed in 1987 and has started limited production runs. The hot cells consist of four hot cells with a stainless steel lining. The chemical separation process of ^{99}Mo from the irradiated Al/Alloy (90% enriched) targets is similar to the process developed by A. Sameh in the Federal Republic of Germany. The product specification conforms very well with the requirements for a safe use in the preparation of $^{99\text{m}}\text{Tc}$ generator for medical use.

On 1985 the Argentine Atomic Commission began the operation of the installation for production of fission Mo-99.

This fact is the result of a project included in the German Argentine agreement, has involving technology transfer to our country of the production method developed by Dr. Sameh Ali at KFK.

The decision of producing fission Mo-99 in Argentine Republic was taken some years ago, because of increasing demand in the medical field for fission Molybdenum generators. The need for Mo-99 has been increasing up to a value of 80 Ci/week at present.

Thus 10 years ago CNEA decided the construction of a suitable plant for fission products processing. This installation, with several modifications, is the one operated at present.

It is placed in a room of 80 m^2 in the radioisotope production plant, next to RA-3 nuclear reactor, allowing in this way a fast and safe transfer of irradiated targets to the processing

hot cell. Four hot cells were settled there: two of them are main, shielded with 20 cm of Pb. Their dimensions are 2 x 1,5 x 1,5 m, being equipped with masterslave manipulators and with double door French system.

The thigh containment boxes are built in stainless steel, with an internal coating of epoxi paint. The other two are auxiliary hot cells equipped with manipulators, and their dimensions are 1 x 1 x 1 m, shielded with 10 cm of lead. The lower part of the cells are used to place several tanks for collection and storage of liquid waste and disposal of gaseous waste.

The engine room was placed in a space between ground and first floor. Later on it will be shown that the characteristics of this installation are varying because of its amplification.

Irradiation targets

The target consists of an Al/U alloy core (UAl_x) with 1 g Uranium enriched to 90%, which is Aluminium-wrapped as a sandwich. It is 13 cm long, 3,6 cm wide and 0,15 cm thick. The weight of Al is 13 gr (each). These targets are produced by the Nuclear Fuel Department of CNEA, employing national technology.

Irradiation conditions

The plates, properly disposed, are placed in RA-3 reactor core, exposed to a neutron flux of $3 \times 10^{13} \text{ n/cm}^2 \text{ sec}$ and using the cooling system of the reactor. Because of the need of changing the reactor core (it is necessary to go from 90% to 20% enrichment) from the beginning of this year the reactor is operating with aged fuel elements, which produce a real flux of about $1,5 \times 10^{13} \text{ n/cm}^2 \text{ sec}$.

The irradiation time of the plates is 5 complete days, and after this they are cooled 16 hours in the reactor pool before transportation for processing.

A tight can is used to contain the irradiated plates for transport from the reactor to the processing hot cell.

Transportation of irradiated targets

The reception of the tight can with the irradiated plates from the reactor and transportation to the processing cells are carried out with a self-propelled shielding specially designed for this purpose. The weight of the shielding is about 2,5 Tn and the thickness of Pb is 23 cm.

As the height of target reception at RA-3 reactor and the height of the entrance system at the cell differ in about 1 m, the position of the shielding door can be varied between those limits.

Lodgement inside the shielding allows a convenient energy dissipation. In order to enter plates in the hot cell, the double door "LA CALHENE" system has been modified, allowing the operation to be made in leak-proof conditions.

Description of the procedure

As can be seen in Fig I the adjustment of operation of the installation was divided in four stages.

The procedure followed for processing the plates is the one developed by Dr. Sameh (Fig. II). At this point, it is convenient the following comments can be made about the equipment employed. Owing to difficulties for getting imported elements, several of them were replaced.

<u>FIRST STAGE:</u>	STARTING OF INSTALLMENT OPERATION	<ul style="list-style-type: none"> * IRRADIATION SYSTEM * TRANSPORT DEVICE FOR IRRADIATED TARGETS * PROCESSING STEPS
<u>SECOND STAGE:</u>	NON COMMERCIAL PRODUCTION CHARACTERIZATION OF FINAL PRODUCT (Mo-99)	<ul style="list-style-type: none"> * RADIONUCLIDIC PURITY * CHEMICAL CHARACTERISTICS AND RADIOCHEMICAL PURITY
<u>THIRD STAGE:</u>	EMPLOYMENT OF Mo-99 IN GENERATOR PRODUCTION (NON-COMMERCIAL PRODUCTION)	<ul style="list-style-type: none"> * BEHAVIOUR OF FISSION Mo-99 IN ALUMINA COLUMNS * CHARACTERISTICS OF ELUTED Tc-99 m * GENERATOR EFFICIENCY AND YIELDING
<u>FOURTH STAGE:</u>	ROUTINE PRODUCTION FOR COMMERCIAL PURPOSES	<ul style="list-style-type: none"> * WEEKLY PRODUCTION OF Mo-99 * LIQUID WASTE DISPOSAL * DISSOLUTION OF IRRADIATED U-235 AND LATER PURIFICATION

* ALL THESE STAGES INVOLVE PERSONNEL LICENSING AND DOCUMENTATION EVALUATION BY THE REGULATORY BODY.

FIG.I

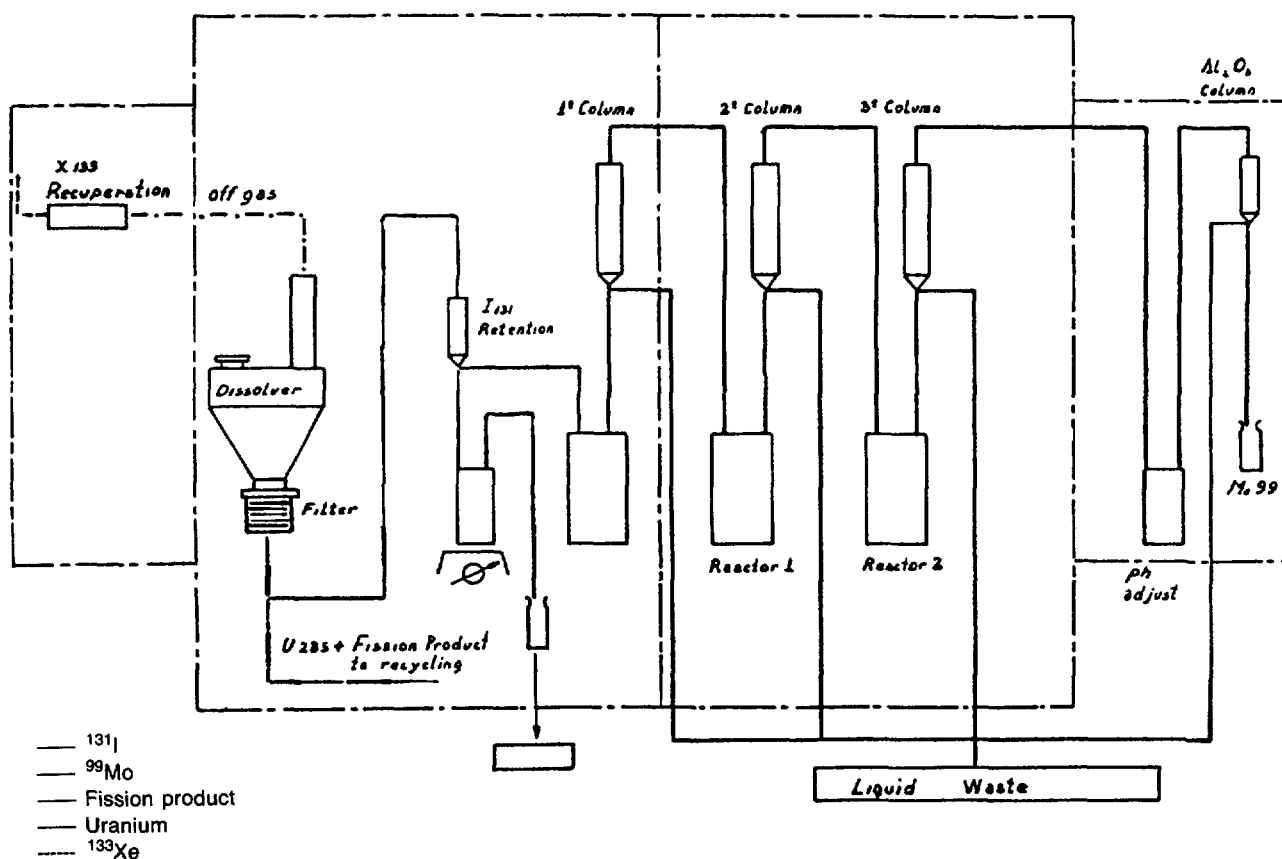


FIG.II

For instance tantalum reactors changed to P.V.C specially molded reactors, with a wall thickness of about 1 cm which allows working in vacuum conditions without any difficulties.

The tantalum or stainless steel valves were replaced by specially designed and built PVC valves. The exchange columns are contained in PVC tubes, also specially designed, to bear the depressure conditions of the process.

In this way, re-changeable elements have disposable characteristics, because the replacing of these elements does not represent an important expense.

The methodology employed involves depressure conditions during almost all the process in order to keep the fission gases in a closed system. The irradiated targets, in the first chemical step, are dissolved in hot alkaline medium with a continuous flow of N_2 .

The solution, after cooling, is filtered through a fritted plate, built in stainless steel.

The insoluble residue contains Uranium as diuranate and Uranium dioxide, together with insoluble fission products such as Ruthenium, Zirconium, Niobium and Lanthanides.

The filtrate contains Molybdenum, together with the Aluminate and the soluble fission products such as I, Te alkaline and alkaline earth cations, Sb (and so on).

At this point we can carry out the recuperation of I-131 with some success.

After the first stage, the purification of Mo-99 is carried out mainly by ionic exchange chromatography. It has been thoroughly studied during the adjustment of the original method, specially loading rate and washing of the columns, in order to reach adequate decontamination factors. As a result of these studies, the

loading, washing and elution rate should not be greater than 8 ml/min to obtain a final product of good quality.

Therefore a first anionic exchange column AG-1 is loaded with the filtrate solution. After washing, the Mo is eluted directly to the second main hot cell to carry out the next step of the purification process: complexing Mo with potassium thiocyanate in acid medium, in order to obtain the well known complex $\text{MoO}(\text{SCN})_4^-$

The purification step following the Mo-SCN complex formation is the passage through a CHELEX 100 resin column in its anionic form, where the complex is retained quantitatively.

After the washing of CHELEX column, the elution of Mo is performed with hot NaOH solution (50°C).

The next step is to repeat the formation of Mo-SCN complex and its passage through a CHELEX 100-200 resin column, with the same washing and elution conditions, to guarantee the purity of the final product.

The whole process is carried out under depressure conditions to avoid the escape of fission gases, whose disposal will be explained later on.

The liquid circulation is carried out during almost all the process by depressure conditions (producing suitable ΔP), if necessary, with the help of pulsating pumps.

With the elution of Mo from the second resin column, the operation in cell II is completed, and the eluate is carried to the second auxiliary cell where pH is adjusted to a value of 3,5 before passing the solution through an Al_2O_3 column, which is the last step of purification.

Washing this column is made with a dilute HNO_3 solution and water, paying special attention to washing rate. Finally Mo is eluted with NH_3 solution in a volume of 30 ml.

Waste Disposal:

a) Gaseous:

1) Dissolution: the H_2 produced during dissolution of Al/U plates in alkaline medium is driven into an oxidation system with CuO at 400°C and the formed water is condensed. The remaining gases (a nitrogen stream permanently carries the fission gases through the system) are collected in pre-evacuated stainless steel tanks (total volume: 400 l). After a week of storage the gases are transferred to four tanks (100 l each) with activated charcoal, placed together with the aforesaid tanks under cell number one.

After another week of storage the gases are carried into 5 tanks (89 l each) with activated charcoal (placed on the top of cell number one) and then they are delivered to the ventilation system of the cells.

A study of separation of Xe-133 by chemisorption is carried out at present in order to obtain high purity Xe.

Mo-SCN complex formation is carried out in a pre-evacuated reactor and is accompanied by pH change from alkaline to acid medium. Produced gases are collected in a 100 l tank under the cell and after a week carried to four tanks (total volume; 320 l) with activated charcoal, placed on the top of main hot cell number 2.

These off-gases are delivered to the ventilation system of the hot cells, which involves fourteen 200 l towers, located in the cellar containing activated charcoal, which can work in series connection or in parallel. After passing these columns the air is forced through a battery of absolute filters.

b) Solids:

The resin columns (AG-1x8 column kept in a leak-proof stainless steel cylinder) as well as valves, quick-connects, hoses, cleaning papers, are taken out of the cell with the french "PADIRAC" system.

c) Liquids:

i) High activity liquid wastes from AG-1 resin loading and washing:

There are two tanks (100 l each) under cell number 2 that allow, in an alternated way, up to 5 months of decay for effluents corresponding to this stage (about 3,5 l per each process including washing solutions).

ii) Medium activity liquid wastes:

Five 100 l tanks allow the storage of liquids coming from CHELEX I and II pre-washing and loading acid washings of cell number II equipment (about 11 l per process) during 5 months.

iii) Disposal after the mentioned decay period:

Liquids (I and II) are disposed by cementation into evacuated leak-proof tanks (200 l).

Chemical and physical characteristics of produced Mo-99

In Fig.III are seen the main contaminants of Mo-99 (obtained).

It is worth mentioning that because of lack of space a final purification step by volatilization of Mo has not been implemented.

- Specific activity: $\geq 10.000 \text{ Ci/g Mo.}$
- Concentration: $> 1.000 \text{ mCi/ml.}$
- Radiochemical purity: ^{99}Mo as Molybdate $> 99\%$
- Radionuclidic purity (with reference Mo-99 activity)

^{131}I	$< 10 \text{ ppm}$
^{103}Ru	$< 20 \text{ ppm}$
^{95}Nb	$< 1 \text{ ppm}$
^{95}Zr	$< 0,1 \text{ ppm}$
$^{132}\text{Te}-^{132}\text{I}$	$< 0,1 \text{ ppm}$
$^{140}\text{Ba}-^{140}\text{La}$	N.D
^{141}Ce	N.D
^{144}Ce	N.D
α	$< 10^{-4} \text{ ppm}$

FIG.III. Product specification of fission molybdenum.

As will be seen later on, at present the installation is being enlarged, which will include this volatilization step, looking for an enhancement of the purity of final process.

The chemical state of (obtained) Mo-99 has been studied by high tension electrophoresis, showing that MoO_4^- (form) is present in more than 99% in the final product.

This material is employed at present for the production of Mo-99/Tc-99m generators with activities of 1 Ci or more.

Besides when studying elution curves and elution response (yield) it can be seen that they greatly overpass these obtained with imported Mo-99, that is employed also in generator production at present.

Comments about production process

After about 40 production processes, it has been demonstrated to be highly reliable and attractive because it avoids tedious operations of separation by extraction or precipitation.

The process yield is greater than 80%, taking into account the theoretical data obtained applying the ORNL "Origen" Programme to our irradiation conditions.

The operation can be carried out in highly reliable conditions.

We have processed from 1 g to 4 g of U-235 without difficulties (each Uranium gram is accompanied by 13 g of Aluminium), without affecting yield. Obtained Mo-99, is suitable for generator production, with a satisfactory response.

U-235 Purification and future building

As we are not allowed to accumulate more than 50 g of U-235 in each cell, we have begun with the dissolution of the precipitate formed during the alkaline treatment of the irradiated targets (the precipitate consists mainly of UO_2 and insoluble compounds).

For this operation we have developed an equipment that allows the transference of the precipitate from the filter to a dissolver and later filtration, obtaining a solution of $U-CO_3^-$ complexes, but at present we do not have enough space to continue the recycling of uranium.

Future facilities:

As I said in the beginning, we are working at present in a place belonging to the Radioisotope Production Plant. During 1986 (the last year) the construction of a special building for this project is being carried out.

The new building covers an approximate area of 600 m² and comprises a processing room with capacity for three new cells. Uranium laboratories, chemical and radiochemical laboratories and dressing room. On the first floor are offices and ventilation engines; filters room in first and second floor.

A communication duct has been prepared between cells in operation at present and those to be constructed in the future in order to work with all the cells in connection. This structure will allow the separation of Xe-133 and I-131, for purification of Mo-99 by volatilization and the completion of the recycling of U-235.

The design of the new cells has been developed, entering now in the acquisition stage of some elements for the construction.

The main difficulty at present is the reactor: owing to the projected change in the core (90% to 20% enrichment) it has to stop for a long period. In order to continue with the present programme, we have begun studies intending to irradiate targets in the reactor of the CNEA in Bariloche (in the south of the Argentina) that can reach a neutron flux of $3 \times 10^{13} \text{ n/cm}^2 \text{ sec}$.

DEVELOPMENT OF THE ^{99}Mo PROCESS AT CRNL

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Abstract

Highly enriched uranium (HEU) is used for Mo-99 production at CRNL. Dissolution of the targets and loading of the solution onto Al_2O_3 columns is discussed. Development work continues to reduce processing time and overall product cost. A process for treating the fission product waste has been selected and a facility for processing is being designed.

Low enriched uranium (LEU) is planned for targets eventually. Our experience with Si-based fuel for targets is poor, and alternatives are being sought.

1. INTRODUCTION

The production of crude Mo-99 at CRNL has grown ten fold over the past ten years. The process is based on that developed at Brookhaven [1] in the 1950's, but a large experience base has built up which is in itself a valuable technology. The Mo-99 is purified via a proprietary process by the AECL Radiochemical Company before it is used in Tc-99^m generators.

Development has focussed partly on cost reduction. Interim waste treatment is being postponed by tank storage, and work is underway to apply processes that have been developed to treat this waste. Finally, conversion of the uranium from 93% enriched in U-235 to 20% enriched in the fuel is anticipated and its influence in the process studied.

2. CURRENT PROCESS

The target is made from U-Al fuel core, the same as used in NRU reactor fuel. Figure 1 shows a photograph of the 15 cm long target with its outer coat of Al with fins, and the target mechanically stripped ready for dissolution.

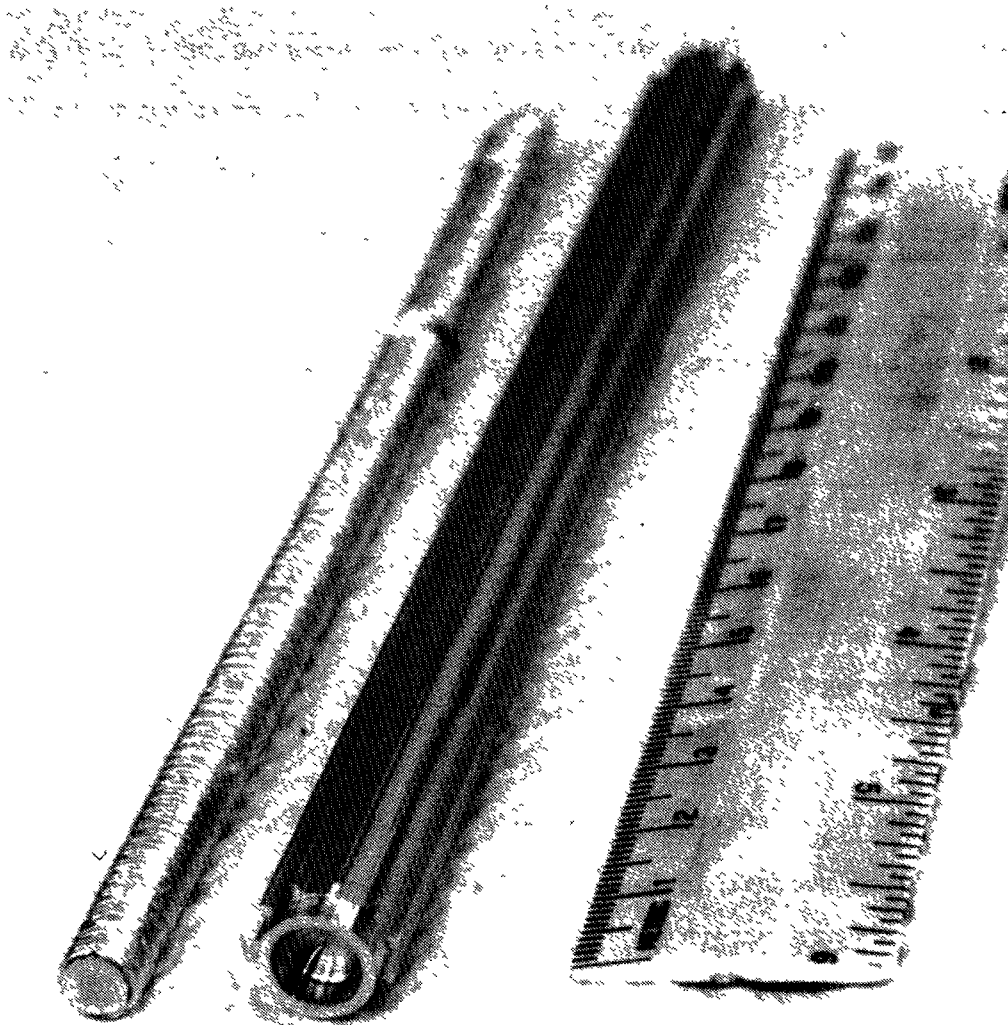


FIG.1. ^{99}Mo targets (HEU).

The targets are assembled into fuel strings and irradiated at a thermal neutron flux $2-3 \times 10^{14} \text{ n/cm}^2 \cdot \text{s}$ for a scheduled period. Figure 2 shows that the Mo-99 content of a target reaches maximum at about 13 days, for the flux conditions noted.

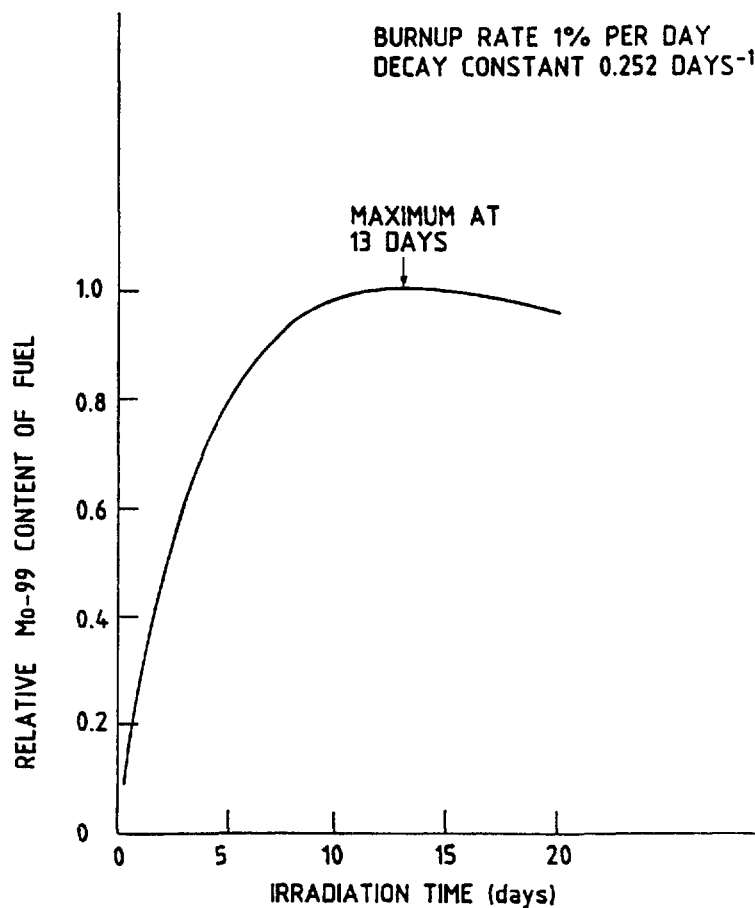


FIG.2. Relative ⁹⁹Mo content of fuel vs. irradiation time.

The recovery process for Mo-99 is outlined in Figure 3. After a short cooling period, the target is stripped and dissolved initially in dilute HNO₃ which contains Hg(NO₃)₂ to assist Al dissolution. Concentrated HNO₃ is added part way into the dissolution to achieve a maximum dissolution rate. The dissolution is rapid and violent. Figure 4 shows the dissolution of 4 unirradiated targets, 15 minutes after the dilute acid was added. Foaming into the reflux condenser is typically observed in glass equipment in the laboratory. About one hour is reserved for dissolution. Water is added to the solution for pH adjustment at the end of the dissolution.

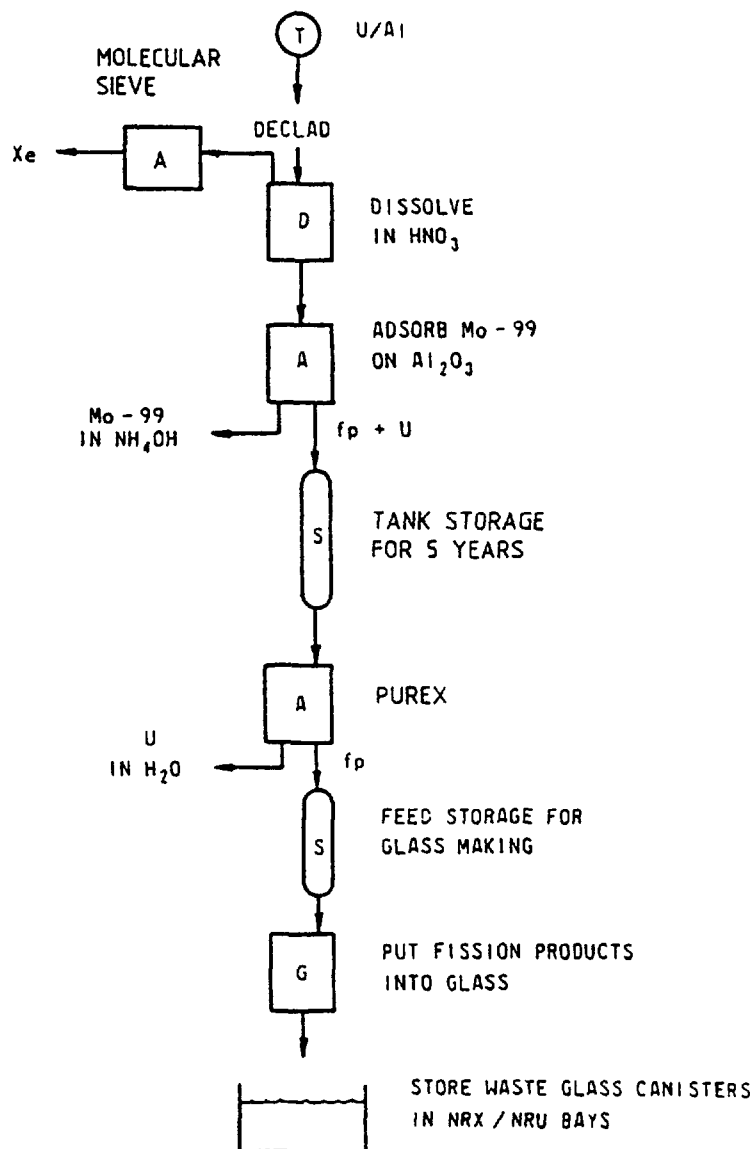


FIG.3. Proposed CRNL process.

The solution is drawn through a glass column containing preconditioned Al₂O₃. The flow rate is monitored closely to prevent channelling of load solution through the bed. Several loadings may be made, depending on the number of targets dissolved.

The column is rinsed with dilute HNO₃, water, then dilute NH₄OH before recovery of the Mo-99 by elution with 1 N NH₄OH. This product is counted by a shielded detector located outside the hot cell, and then shipped to the AECL Radiochemical Company for further purification and distribution.

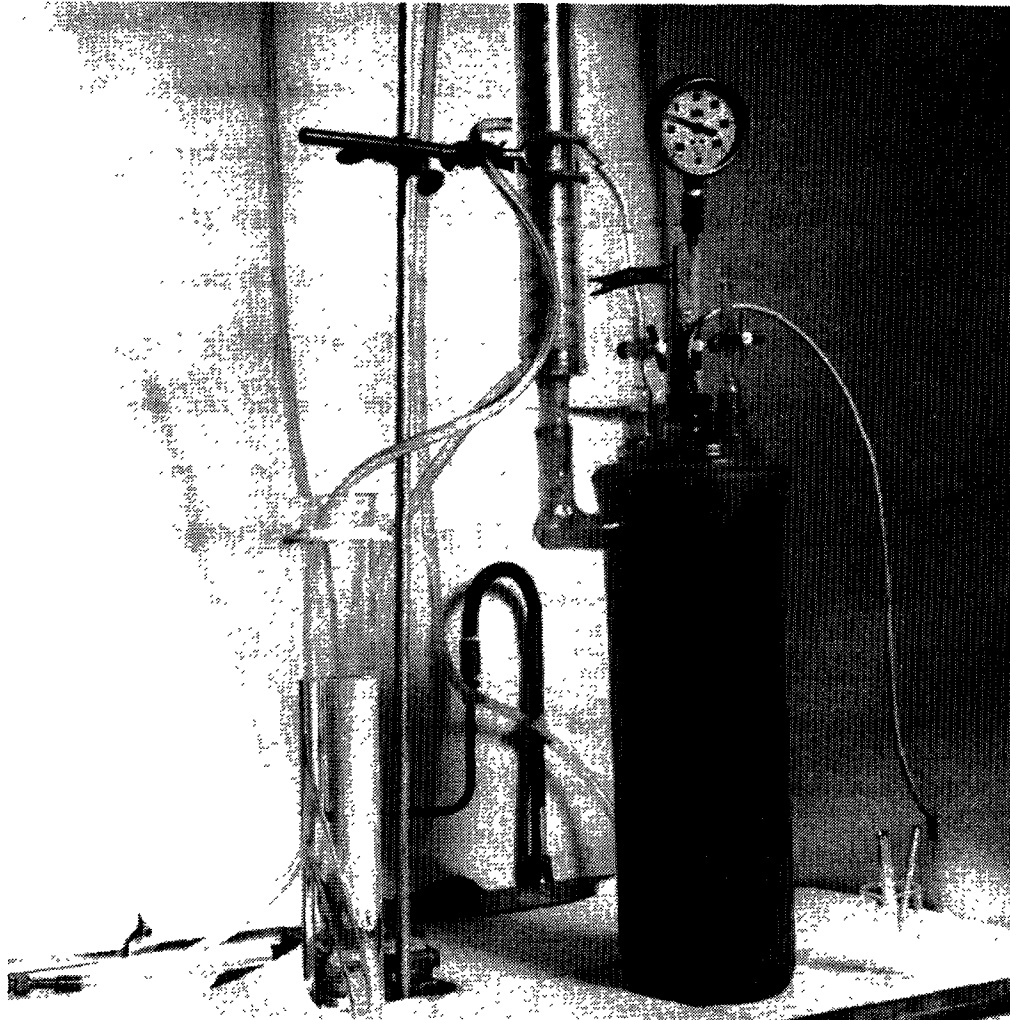


FIG.4. Dissolution of four targets: $\theta = 15$ min.

Waste solution at a predetermined pH and uranium concentration is sent to a 24000 L tank for storage.

3. PROCESS DEVELOPMENT

Targets, processing, and waste treatment will be discussed.

3.1 HEU Targets

There has been little need for target development. A proven fuel design was used and other than making targets long (to their present length) to get more target length into a given length of reactor core, no work has been necessary.

However, aluminum is the major component of the targets, both in the U-Al alloy and in the cladding, so it is a major waste product. The aluminum clad is stripped mechanically to within a millimeter of the core. Complete removal of the clad is not attempted to avoid gouging the U-Al core and losing the Mo-99. Cutting wheels were used in the laboratory on unirradiated targets to remove clad completely by stripping lengthwise, as shown in Figure 5. Unfortunately, irradiation of the target makes the clad bond very firmly to the U-Al core and the clad cannot be removed this way. A suitable coating for the core that would prevent this bonding may be possible, but this has not been pursued.

3.2 Process Development

Process development has had two goals:

- (i) decreasing processing time
- (ii) maximizing Mo-99 recovery.

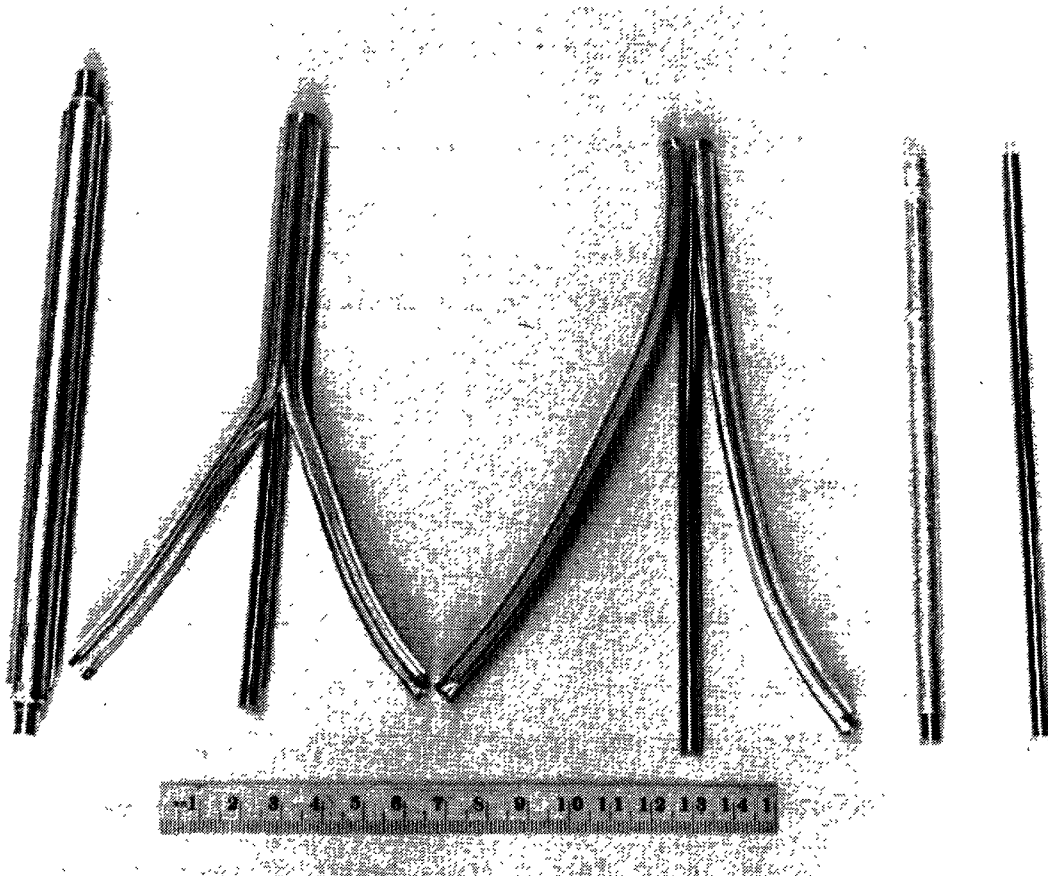


FIG.5. Longitudinal stripping of targets.

Presently, eight targets are dissolved together in the dissolver. The dissolver diameter has been limited to less than 15 cm for criticality concerns. Dissolving more targets per batch using the current dissolution recipe causes foaming past the condenser into off-gas scrubbers. Thus, Mo-99 is lost. The dissolution rate depends on the volume of dilute HNO_3 used to start the reaction and can be controlled also by the addition rate of the concentrated acid. This avoids foaming through the condenser. The current tall stainless steel dissolver has a water jacket for additional control of the reaction. Maintaining the cooling water flow throughout a dissolution gives a black solution due to UAl_4 particles still undergoing dissolution. This solution plugs the Al_2O_3 column quickly. Eventually, the particles dissolve and processing can begin.

The overall processing rate is currently limited by the flowrate through the Al_2O_3 column. Doubling the rate gives channelling through the bed. A larger diameter column with more Al_2O_3 does not channel at the higher flow rates, but there is irreversible sorption of Mo-99 on the Al_2O_3 and this loss goes up with more Al_2O_3 in the bed. A column with a large cross section for flow, but with a shorter path length so that the quantity of Al_2O_3 does not change may be acceptable but has not been tried. An alternative is to reduce the volume of load solution by reducing the quantity of dilution water added to the dissolver. This approach has been successful; loading rates have remained unchanged but the quantity of solution loaded has been reduced.

Measured Mo-99 recoveries are compared with prediction of the amount that should have been in the targets. This prediction takes reactor flux and shutdowns into account. Ratios of actual yield to theoretical yield were often less than 50%. However, mass balances were made around the process by actually taking highly diluted solutions out of the processing cell. These balances showed yields were near 90%, thus the computer code

is in error but still used as a guide; inadequate knowledge of the thermal neutron flux along the targets is thought to be the problem.

Laboratory work showed that load solution pH should be the single most important variable affecting yield. Figure 6 shows that too acid a solution gives poor retention (leakage) on the Al_2O_3 column and Mo-99 is found in the load solution after it has gone through the column, with a fixed irreversible adsorption on the Al_2O_3 that elution with NH_4OH cannot remove. The conductivity of the eluted solution is measured after passing through the Al_2O_3 column. Experience with the dissolution process gives a solution conductivity that varies little from run to run and the dissolution recipe has been optimized to give maximum Mo-99 recovery.

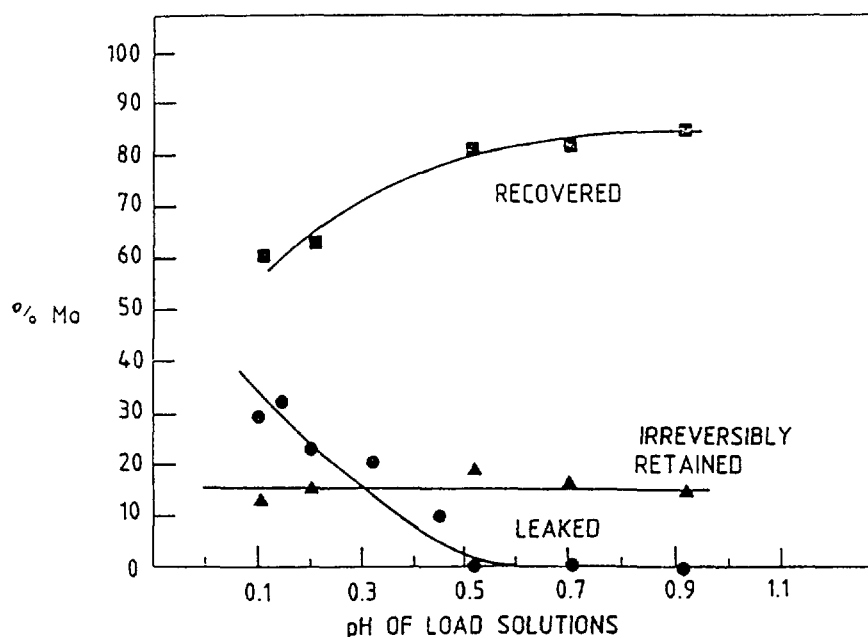


FIG.6. Mass balance for molybdenum on alumina as a function of pH.

Despite these efforts to increase process efficiency, there are occasional process upsets. One major one is the occurrence of some partially dissolved targets after one hour of dissolution. Clearly, their dissolution rate is lower than other targets from the same rod, or all the

targets in a rod may be affected. Undissolved targets are recycled to the next dissolution and those after the last dissolution are disposed of, thus their Mo-99 is lost. Tests on irradiated NRU fuel taken to 90% burnup show a very low dissolution rate. These tests were extended across the range 0 to 90% burnup and give the results shown in Figure 7. A small increase in burnup of Mo-99 targets can lower their dissolution rate dramatically. The mechanism has yet to be determined, and more data are needed on the steep portion of the curve.

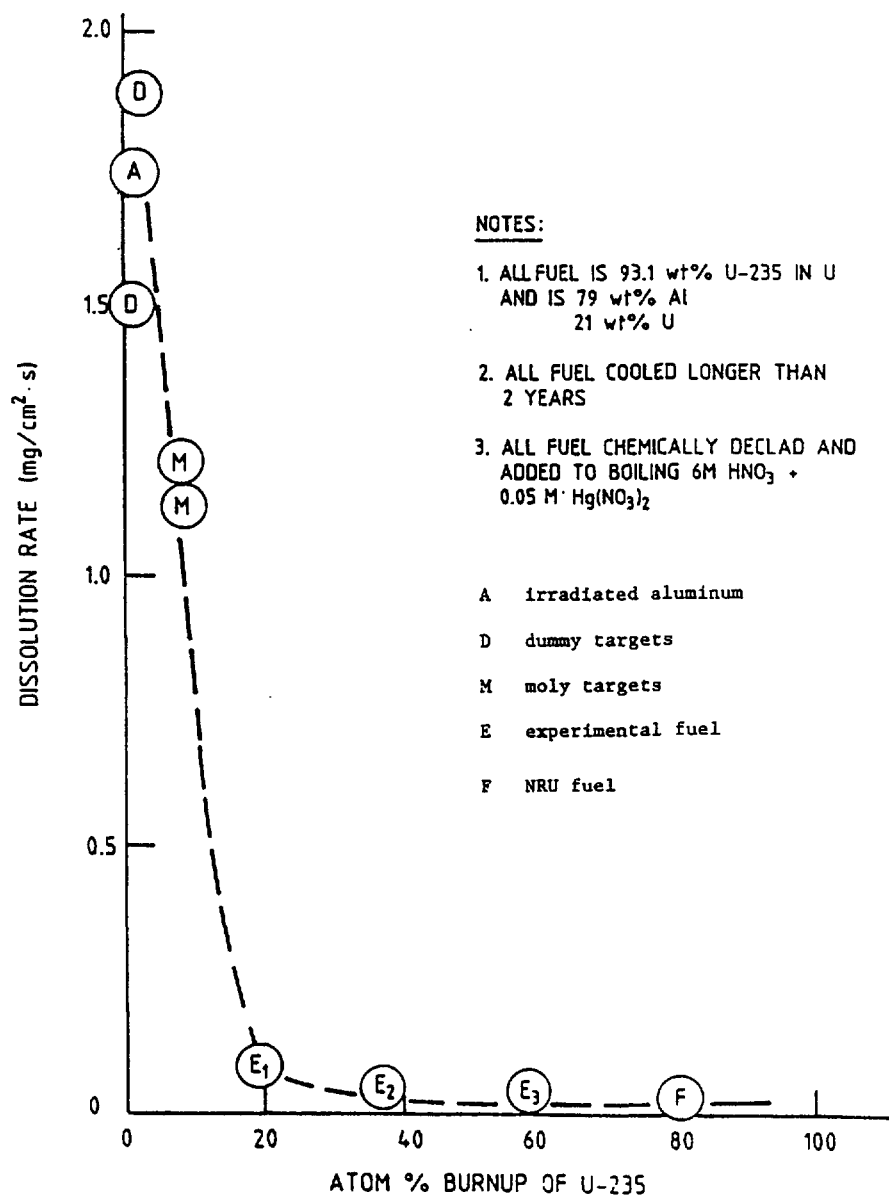


FIG.7. Effect of fuel burnup on dissolution of UA1 alloy.

3.3 Waste Treatment

The treatment of the highly radioactive fission product solution after Mo-99 recovery has been a major concern. Early attempts to recover the uranium by column adsorption were stopped because of criticality concerns; there was a relatively poor uranium mass balance around the process. Then, for many years the solution was cemented in 20 L pails and stored below ground. This waste poses a problem for eventual disposal because of the highly enriched uranium present which will likely have to be recovered. Laboratory tests have demonstrated 99% extraction of uranium from simulated cemented waste. These tests are the basis of a process that could be developed.

Currently, the waste solution is stored in a large tank, with sufficient capacity for five years of liquid. A hot cell is planned in which mixer-settlers will be used to recover the uranium using the Purex process. Campaigns are planned in which two years would be used for uranium recovery, then glass-making equipment would be installed to vitrify the waste from the Purex process to give a sodium borosilicate glass with 20 wt% Al_2O_3 and a small fission product content. The latter process has been demonstrated on fully radioactive solution and is being scaled up. An alternative to vitrification is extraction of saleable radioisotopes such as Cs-137, Sr-90, Pm-147, Ce-144 and Ru-106 which will be added to AECL's list of radioisotope products. The waste would then be suitable for bituminization in the existing facility at CRNL. Extraction processes for the latter four radioisotopes have been developed and used on such solution. An ion exchange process for Cs-137 recovery seems likely.

4. LOW ENRICHED URANIUM (LEU) TARGETS

The supply of HEU (93% enriched U-235) for research reactors such as NRU will eventually be curtailed by the U.S. For that reason, fuel for reactors is being developed using LEU (20% enrichment) as the alternative. To keep costs down, LEU targets for Mo-99 production should use reactor fuel. A fuel for NRU is being tested using uranium-silicon alloy powder that is mixed and alloyed with Al to give U_3SiAl . The Si reduces core swelling at the high uranium burnup necessary for reactor fuel.

Targets were made from this fuel and they dissolved in the laboratory normally. The Si formed a fine slurry of SiO_2 . These particles were removed using ordinary paper filter to prevent plugging of the Al_2O_3 column. Recovery of Mo from Mo-99-traced solution was as high as with the usual UAl targets. However, irradiation of the LEU targets produces a much smaller SiO_2 particle that is not filtered effectively by paper. Filtered solution still plugs the Al_2O_3 column eventually. Recovery of Mo-99 from the column is relatively poor, sometimes only 50% of that expected from HEU UAl targets. Adsorption of Mo-99 on the SiO_2 surface is suspected for the poor recoveries. This was not detected in the laboratory, perhaps because the surface area of the SiO_2 from irradiated fuel is much higher than from unirradiated fuel. Even if the SiO_2 could be removed from the load solution, the loss of Mo-99 by adsorption of the SiO_2 would be unacceptably high.

Alternative LEU targets are being sought. Since Mo-99 targets need only go to low uranium burnup, the need for Si is questionable. A U/Al core has been made from finely powdered uranium metal dispersed in aluminum. A second one was made with a UO_2 /Al core. These cores will be processed in the laboratory to check for difficulties with dissolution and

Mo-99 recovery. If satisfactory, targets will be made with LEU and processing done after irradiation.

5. SUMMARY

Processing of HEU targets at CRNL has been reviewed. Targets are made from fuel prepared for NRU reactor. Dissolution after irradiation usually yields clear solution after one hour, but a UAl_4 slurry or undissolved targets are sometimes found. The latter may be caused by a higher burnup than normal.

REFERENCE

- (1) Stang Jr. L.G., "Manual of Isotope Production Processes in Use at Brookhaven National Laboratory", BNL-864 (1964).

PRODUCTION TECHNIQUES OF FISSION ^{99}Mo

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Abstract

Generally two different techniques are available for molybdenum-99 production for use in medical technetium-99 generation.

The first one is based on neutron irradiation of molybdenum targets of natural isotopic composition or enriched in molybdenum-98. In these cases the Mo-99 is generated via the nuclear reaction $^{98}\text{Mo} (n, \gamma) ^{99}\text{Mo}$.

Although this process can be carried out at low expenditure it gives a product of low specific activity and, hence, restricted applicability.

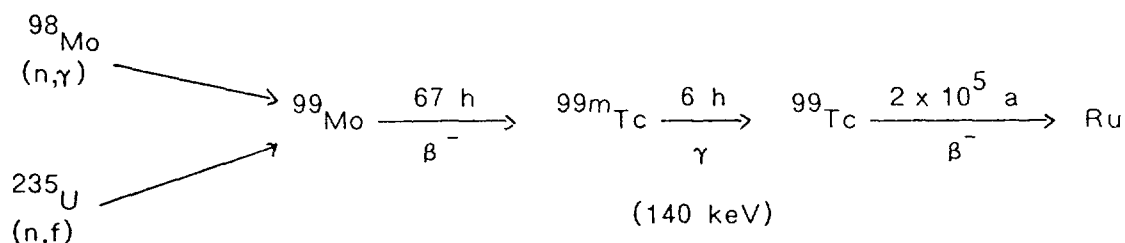
In a second process Mo-99 is obtained as a result of the neutron induced fission of U-235 according to $^{235}\text{U} (n, f) ^{99}\text{Mo}$.

This technique provides a product with a specific activity several orders of magnitude higher than that obtained from the $^{98}\text{Mo} (n, \gamma) ^{99}\text{Mo}$ nuclear reaction and perhaps even more important up to several thousands curies of Mo-99 per production run.

In this paper a modern production procedure of Mo-99 via the fission reaction, which was developed at the Institute of Radiochemistry of the Nuclear Research Center Karlsruhe will be described. The targeting, irradiation of U-235, the separation and purification steps involved as well as the recycling of the non-converted U-235, which should be a major consideration in any production technique, will be discussed.

INTRODUCTION

As shown below two basically different approaches can be used to produce Mo-99 the precursor of Tc-99m, i.e. either via the $^{98}\text{Mo} (n, \gamma) ^{99}\text{Mo}$ nuclear reaction or by the neutron induced fission of U-235 according to $^{235}\text{U} (n, f) ^{99}\text{Mo}$.



In order to decide which one of these two reactions can provide the best source for the technetium required in nuclear medical studies one has to keep in mind that the overriding consideration in the application of Tc-99m as a diagnostic tool in nuclear medicine is the availability of Tc-99m with high specific activities. Only by using Tc-99m with high specific activity a good counting statistic and thus adequate accuracy can be achieved in diagnostic investigations.

A second important aspect is that the chosen technique is capable of providing relatively large quantities of Mo-99 and thus Tc-99m. Only under these conditions one could expect that the product is continuously and professionally tested by highly trained staff and the quality assured. The introduction of highly sophisticated kits, that require ultrapure Tc-99m product with extreme high specific activity has even raised the demands in that respect. Therefore, the two techniques should be discussed in light of these criteria.

The irradiation conditions as well as the specific activities which can be obtained by these procedures are shown below. Clearly only the fission reaction can provide sufficiently large amounts of Mo-99 at high specific activity.

1. Production of Mo-99 via $^{98}\text{Mo} (n, \gamma) ^{99}\text{Mo}$

High flux reactor irradiation:

Natural molybdenum target 1 Ci Mo-99/g Mo

Enriched molybdenum target 10 Ci Mo-99/g Mo

2. Production of Mo-99 via $^{235}\text{U} (n, f) ^{99}\text{Mo}$

Reactor irradiation < 10 000 Ci Mo-99/g Mo

Whether or not Tc-99m of high specific activity can be derived from n, γ produced Mo-99 /ref. 1-4/ will depend on finding an effective technique for separating the Tc-99m daughter activity from Mo-99. Three basically different methods are available:

- Chromatography

The neutron irradiated target (U-235 or Mo-98) is dissolved and after suitable purification steps the Mo is fixed on an alumina bed. The Mo-99 isotope decays to Tc-99m which is eluted by passing physiological saline through the bed.

- Sublimation

The neutron irradiated Mo-target (MoO_3) containing Mo-99 is heated in a furnace in a stream of oxygen up to 850 °C at which temperature the Tc-99m sublimes probably as Tc_2O_7 .

- Solvent extraction

The neutron irradiated Mo-target is dissolved and Tc-99m extracted from the alkaline aqueous solution using methylethyl ketone.

While sublimation and extraction techniques can in principle provide Tc-99m of high specific activity from n, γ produced Mo-99, although the absolute amounts might be relatively small, the chromatographic technique presents inherent problems if Mo-99 of low specific activity is used. They are due to the fact that the low adsorptive capacity of alumina, the most commonly used generator bed material, requires the use of a large bed when low specific activity Mo-99 is employed, conversely with nearly carrier-free fission Mo-99 the bed size may be minimized (5 Ci Mo-99 / g Al_2O_3). An elution profile versus alumina bed weight which demonstrates the fact that solutions of Tc-99m with high specific activity can be obtained only from generators with a small bed volume has been reported by Boyd /1/. Unless new generator types can be developed this restriction will exist.

Taking further into account the problems involved with the sublimation and extraction generators such as corrosion, possible fire hazards with organic extractant, presence of polymeric organic residues especially when as it would be the case at smaller hospitals no adequately chemically trained staff might be available the chromatographic generator loaded with high-specific activity Mo-99 is the only alternative. Thus in the following details of modern production techniques of Mo-99 from the fission of uranium will be discussed including procedural steps for the recycling of the non-converted U-235.

MOLYBDENUM-99 PRODUCTION FROM THE FISSION OF URANIUM

Molybdenum-99 is a product of the fission of uranium according to $^{235}\text{U} (n,f) ^{99}\text{Mo}$. The fission yield of this reaction is 6.1 %. The generated product is diluted by the stable molybdenum isotopes Mo-97, Mo-98 and Mo-100. Their total fission yield is 18.1 %. Nevertheless, the specific activity of molybdenum produced by fission is more than 1000 times higher than that obtained by (n,γ) -process, appropriate cooling and processing time are taken into account.

The production process of fission molybdenum is in comparison with the n,γ activation of Mo-98 quite sophisticated. Different aspects have to be taken into consideration as the targeting, irradiation condition, the extremely high radiation dose, the offgas filtration, product quality, target material recycling, waste treatment and safeguard regulations.

The first chemical process for separation of curiequantities of Mo-99 was described by the Brookhaven group /5/.

In this process the target (93 % enriched U-235 alloyed with Al) was dissolved in 6 M nitric acid catalyzed by mercuric nitrate. Then, after the addition of 0.5 mg tellurium carrier, the solution was passed through an alumina column which selectively absorbed the Mo-99 and the radiotellurium fission products. The uranium and the unabsorbed fission products were removed from the alumina by subsequent washing with 1 M HNO_3 , water and 0.01 M NH_4OH . The Mo-99 was then recovered from the column by elution with 1 M NH_4OH .

Richards /6/ subsequently added a final purification step whereby the Mo-99 was reabsorbed onto a strong anion exchange resin, washed to remove the trace radio-impurities and then eluted with 1.2 M HCl.

Another process based on the extraction of molybdenum in organic solution was developed in Oak Ridge /7/. This method exploits the extractability of molybdenum from acid solution by di(2-ethylhexyl)phosphoric acid dissolved in an inert organic diluent. After separating the organic layer and washing it with 1 M HCl, the Mo-99 is stripped out using a 0.1 M HCl -2 % H_2O_2 mixture. After reacting with sodium nitrite to destroy any residual hydrogen peroxide, the Mo-99 solution is adjusted to 1 M HCl and an identical extraction sequence carried out in new equipment.

Kawakami /8/ has described a variation on this process where, after two extractions and back-extractions, an acid solution of the Mo-99 is loaded onto an alumina column; after washing, a radionuclidically pure Mo-99 is eluted with ammonia.

Molybdenum-99 may also be extracted from a nitric acid solution of fissioned uranium by acetylacetone in carbon tetrachloride /9/, back extraction being achieved with ammonia. Yet another variation of the Mo-99 extraction method has been described by Sivaramakrishnan et al. /10/. In their method the Mo-99 is separated from the uranium and mixed fission products by precipitation with α -benzoin oxime after the addition of molybdenum carrier; to prevent the co-precipitation of the radionuclides oxalic acid is added. The Mo-99 α -benzoic oxinate is purified via a multistage process involving

- the dissolution of the precipitate in ethyl acetate,
- the back extraction of the Mo-99 into 6 M ammonia,
- after iodide carrier addition the extraction of radio-iodines into carbon tetrachloride,
- the precipitation of insoluble hydroxides by ammonia after the addition of iron and zirconium carrier,
- the precipitation of the radio-strontiums after the addition of strontium carrier by ammonium carbonate, and finally
- the reprecipitation of the Mo-99 with α -benzoin oxime.

Arino and Kramer /11/ described a separation method for molybdenum from sulphuric acid on silver-coated carbon granules. In this process the irradiated uranium dioxide is dissolved in a mixture of 2 N H_2SO_4 and H_2O_2 ; after dissolution H_2SO_3 is added to destroy the residual H_2O_2 .

The solution is then added to a column of silver-coated charcoal which selectively extracts the Mo-99 from solution. After the column is washed with a small volume of water, the Mo-99 is eluted with 0.2 M NaOH. Gamma spectrometric analysis has shown that the radionuclidic purity of the Mo-99 is greater than 99 %, but that contamination by Te-132, I-132 and Ru-103 is also evident. The impurity levels, though small, would demand that the Mo-99 made by this process be further purified before being used for generator manufacture.

All processes reviewed are generally able to deliver molybdenum with reasonable purity but highest quality is only available by a combination of them. In addition to these procedures important aspects of running an economical process as well as target material recycling and waste treatment have been neglected.

Thus in the following a new complete fission Mo-99 process cycle with integrated nuclear fuel recycling, target fabrication and management of the radioactive waste will be described.

It has been developed at the Institute of Radiochemistry at the Nuclear Research Center Karlsruhe and demonstrated for two years in weekly production phases on the kCi-scale.

The targets consist of an aluminium clad uranium/aluminium alloy of the approximate composition UAl_3 ; since the aluminium content in the compound is variable, the term UAl_x is mostly used. To achieve the highest possible fission product yields uranium enriched to 90 - 93 % is used. The individual plates are irradiated jointly in one rig exposed to thermal neutron fluxes of approximately $5 \times 10^{13} - 1 \times 10^{14} \text{ n/s cm}^2$ for five to ten days with forced cooling. Figure 1 shows a picture of the fuel element plates in the irradiation holder.

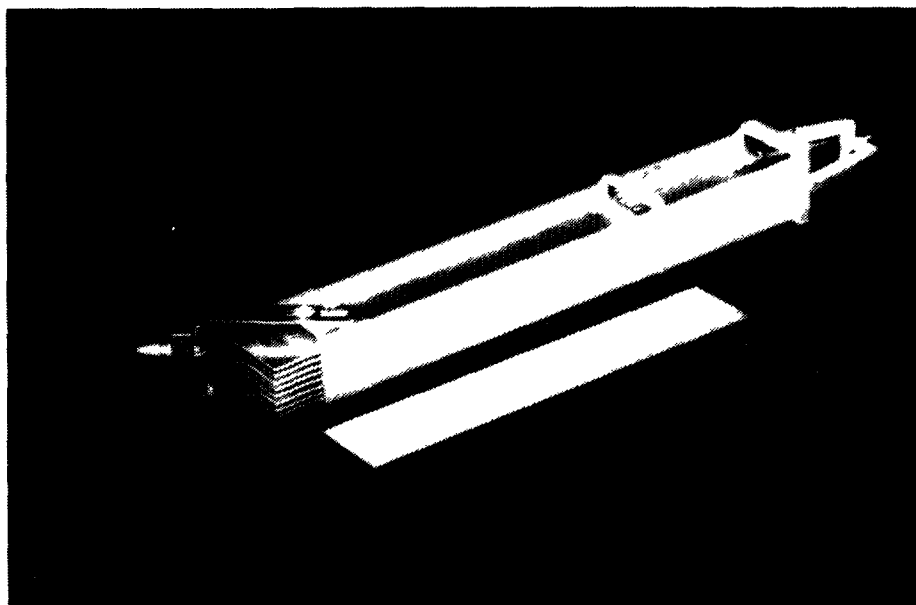


Fig. 1 Fuel element targets in the aluminium irradiation holder. The dimensions of the plates are: 220 mm length, 40 mm width and 1,3 mm in thickness. The dimension of the fuel meat inside is 200 mm in length, 300 mm in width and 0.5 mm in thickness

To minimize the decay losses of the desired nuclide the targets, after a minimum decay period of about twelve hours, are transported to the processing plant. The first chemical step normally consists in the alkaline digestion of the target using 3 - 6 M NaOH respectively KOH.

Figure 2 shows a simplified scheme of the complete Mo-99 production process including the subsequent recycling of nuclear fuel, developed at the Institute of Radiochemistry at KfK.

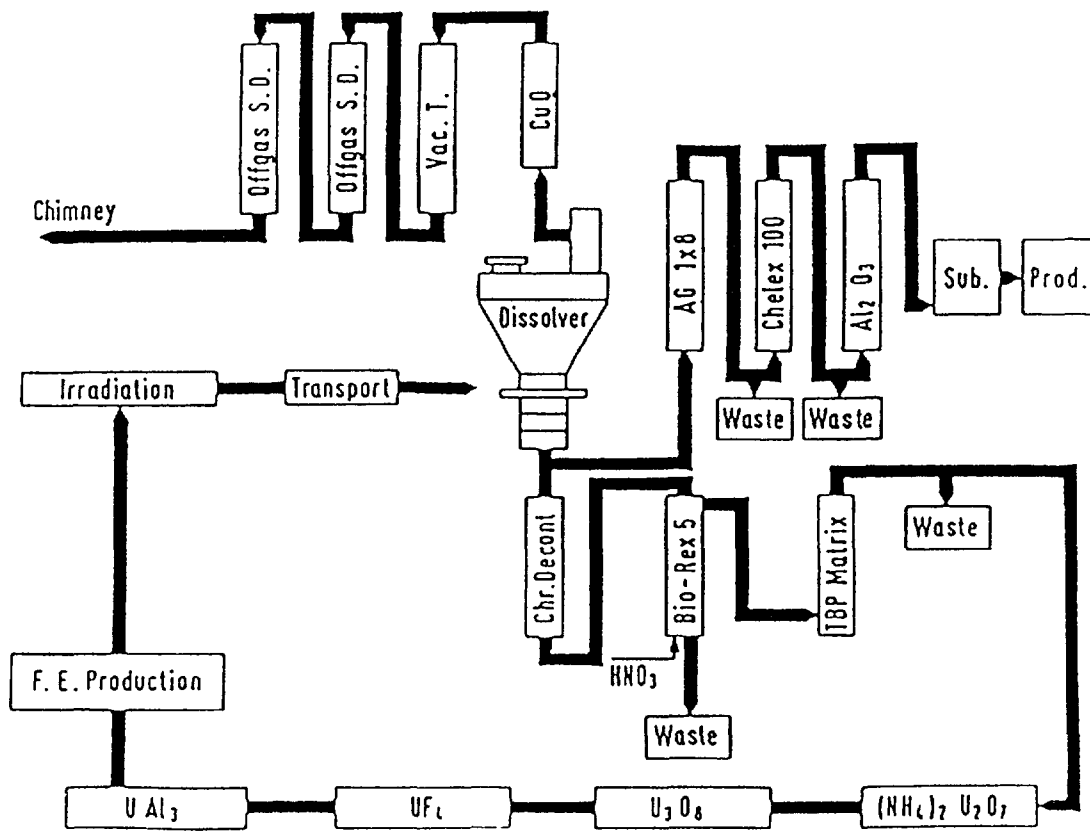


Fig. 2 Scheme of the complete Mo-99 production including fuel recycling and target fabrication

During the alkaline digestion the main constituents of the plate are dissolved namely aluminium and the fission products soluble in this medium such as alkaline and alkaline earth cations as well as antimony, iodine, tellurium, tin, and molybdenum. The volatile fission products with Xenon-133 as the main carrier of activity leave the dissolver at its upper end passing through a reflux condenser together with the hydrogen generated in the digestion process and driven by a nitrogen stream. The hydrogen is oxidized to H_2O via CuO at $350 - 400\text{ }^{\circ}C$ and the resulting water condensed. Xenon is collected together with nitrogen in the preevacuated stainless steel tank and later on carried to the xenon delay section (D.S.) passing deep bed carbon filters. To guarantee a safe, leakage-free process all equipment used in this extremely hot part of the process are made of stainless steel. Figure 3 shows a picture of the digestion equipment [12] and the first Mo-purification column.

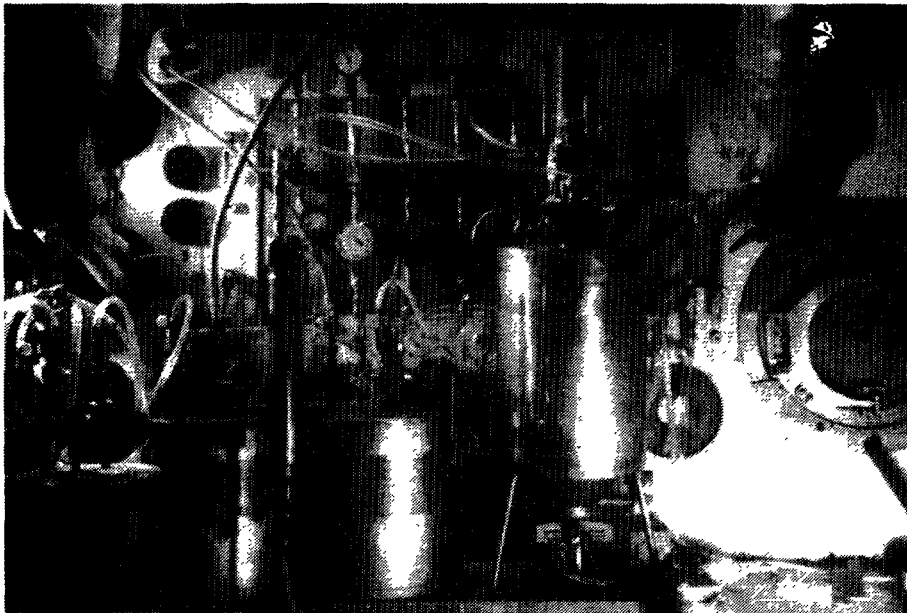


Fig. 3 Stainless steel digestion equipment and the first Mo-purification column in operation in the hot cell.

The alkaline solution containing molybdenum passes through a column of the strong basic exchanger AG1 x 8, 50 - 100 mesh. Molybdenum is quantitatively adsorbed on the exchanger together with a significant part of fission products. Cationic impurities as caesium, strontium, and barium pass through the column together with hydroxaluminat, tellurit and iodine anions. After washing the column with sodium hydroxide molybdenum and the main part of the accompanying fission products are eluted with 1 - 1.5 M sulfuric acid and subsequently with a solution of 0.5 M ammonium hydroxide and 1 M sodium sulfate. This solution is transferred to the Mo-purification cell. The Mo containing solution is collected in a tantalum tank. The adjustment of the process solution for the following purification is carried out in a glove box. A picture of the purification cell is shown in figure 4.

The process solution is subsequently treated with solutions of ammonium thiocyanate, potassium iodide, sodium sulphite and finally acidified with sulphuric acid up to a 1.5 - 2.0 M H_2SO_4 . Under these conditions the molybdenum will be reduced and forms an extremely stable anionic $[Mo(SCN)_6]^{3-}$ -complex with the thiocyanate ions. From this medium molybdenum can be retained quantitatively on ion exchangers with functional nitrilodiacetate groups such as chelex-100 with a distribution coefficient of about 10^4 (13).

In figure 5 the distribution coefficients of molybdenum on chelex-100 in thiocyanate, sulphite and HCl respectively H_2SO_4 containing solutions are shown.

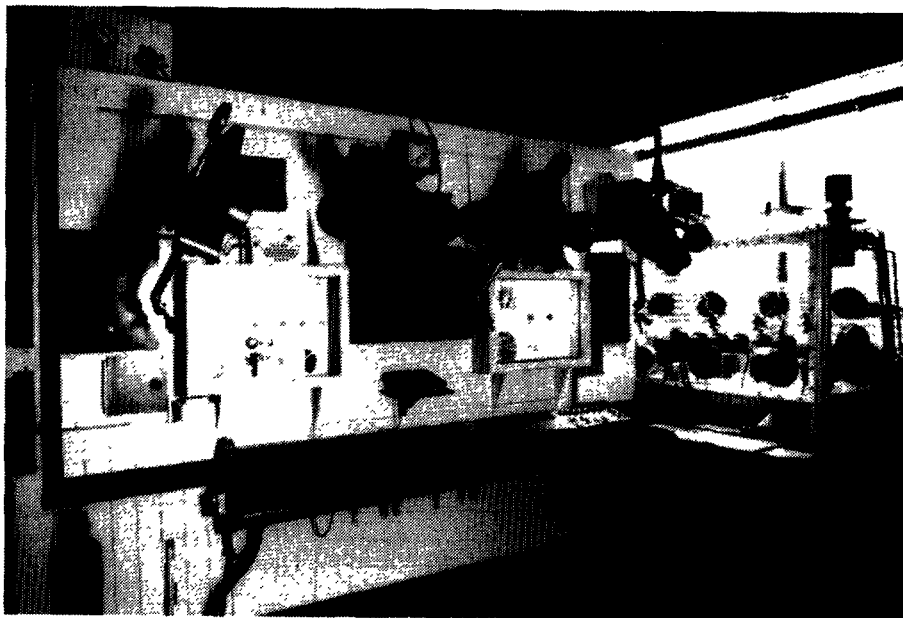


Fig. 4 General view of the fission molybdenum purification cell used in Karlsruhe

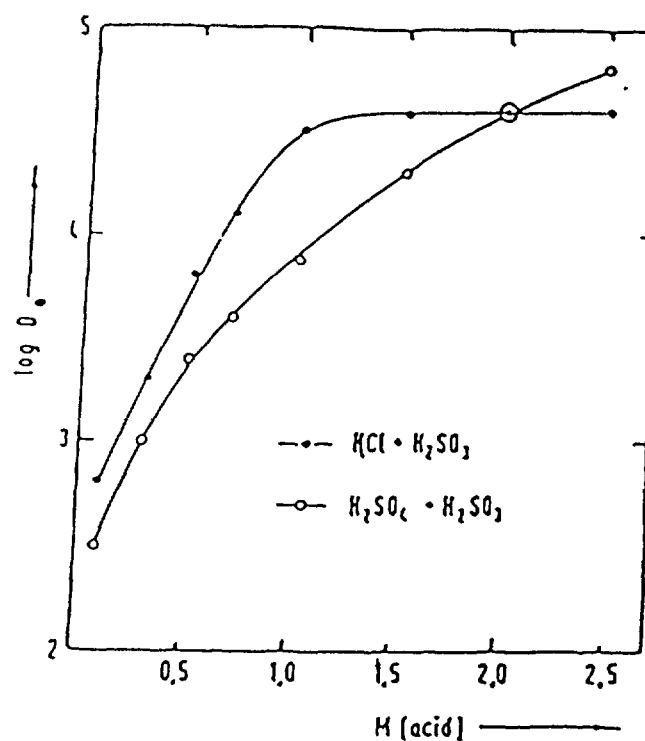


Fig. 5 Distribution coefficients of molybdenum thiocyanate complex as a function of the acid concentration on Chelex-100 50 - 100 mesh

It should be mentioned that under these conditions all fission products which accompany the molybdenum have a distribution coefficient of approximately 1 on chelex-100 that means, in one column a decontamination factor of about 10^5 can be gained without difficulties.

In the following step the column is subsequently washed with thiocyanide containing sulphuric acid, pure sulphuric acid and water. The molybdenum elution from the column is carried out with 1 M NaOH. To guarantee a product of highest purity the procedure is repeated on a second smaller chelex-100 column. The described process is schematically presented on figure 6. The eluate of the second column will be acidified with the calculated amount of nitric acid to adjust a pH-value of the solution between 1.8 - 3.5.

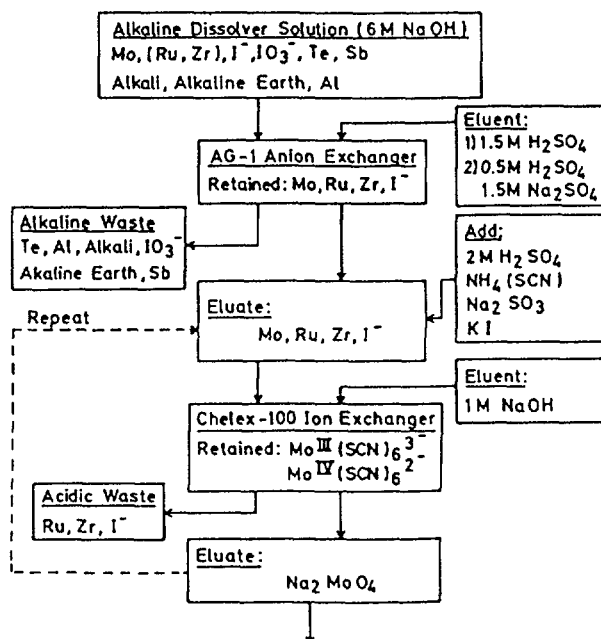


Fig. 6 Flowsheet of the KfK fission molybdenum separation process, the Chelex-100 purification carried out twice.

To avoid retention of corrosion products from the metal equipment on the Al_2O_3 column the solution has to pass first a cation exchange AG 50 x 8 100 - 200 mesh column before it enters a chromatographic column filled with aluminium oxide. The Al_2O_3 -column is useful to purify molybdenum from nonvolatile sodium salts and from possible traces of contamination. After washing the column with 0.01 M HNO_3 and finally with water, the molybdenum is eluted with 1 M ammonium hydroxide. The ammonium molybdate solution is transferred to the sublimation cell via a stainless steel pipe. The molybdenum solution is evaporated in a stainless steel apparatus and afterwards placed into a platinum crucible. The residue is evaporated on an electric hot plate and the crucible with the completely dried residue slowly heated up to about 700 °C in a quartz glass apparatus inside a resistance furnace. At this temperature all organic impurities possibly introduced from the ion exchangers into the product are removed. The last process is the sublimation of the molybdenum oxide. The sublimation is started after a quartz glass condensation device is placed over the

quartz vessel in the furnace and the temperature increased to about 1150 °C. The molybdenum volatilization is finished in about 30 minutes. In the upper parts of the quartz device the molybdenum trioxide is deposited. After removal of the platinum crucible the oxide is dissolved with ammonia vapour. The molybdenum solution is mixed with sodium hydroxide and ammonia is removed by boiling. The solution obtained in that way represents the final product. The flowsheet of this process part is shown on figure 7.

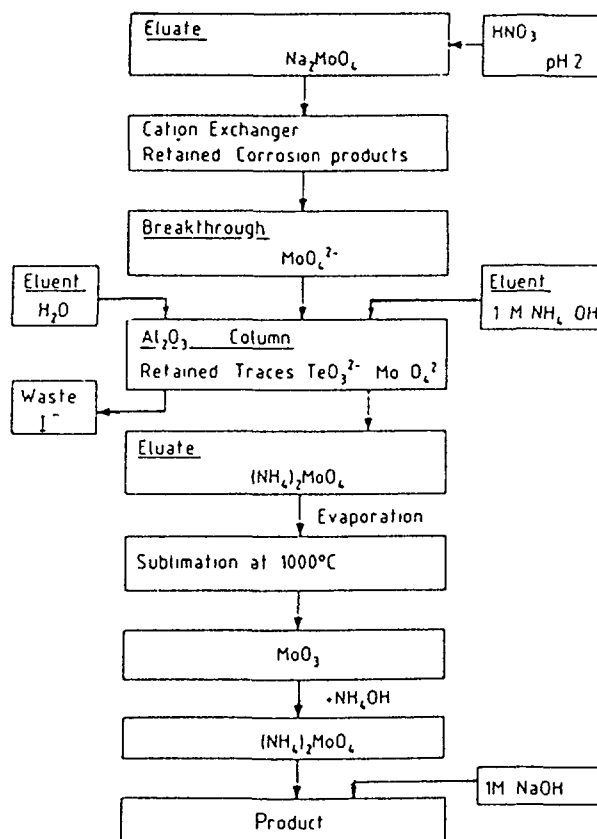


Fig. 7 Flowsheet of the last purification procedure on cation exchanger / aluminium oxide system and the MoO₃-sublimation

The following table shows two typical quality analyses in comparison with the impurities tolerated by the european pharmacopoeia:

Impurity	¹³¹ I	¹⁰³ Ru	¹⁰⁶ Ru/Rh	⁹⁵ Zr	⁹⁵ Nb	¹²⁵ Sb	¹³⁷ Cs	α	⁸⁹ Sr and ⁹⁰ Sr,resp
Limit values according to P.E.	50	50	the rest of emitters together 100 ppm					10 ⁻³	0,6 and 0,06
KfK									
molybdenum	0,11 0,081	0,28 0,21	0,0084 0,0051	- -	0,0035 0,007	0,0021 0,0046	- 0,00008	5x10 ⁻⁵ 4x10 ⁻⁵	2x10 ⁻⁵ 3x10 ⁻⁵

Foreign Nuclides Related to ⁹⁹Mo at Time of Calibration in ppm

The advantages of the described process are:

- reproducible highest product quality with regard to any chemical impurities and to the specific activity
- economical and safe offgas treatment because all the purification columns which are employed operate with solid absorbers and not inflammable or corrosive diluents.
- The waste streams are clearly divided into high, intermediate and low active streams. Due to the alkaline digestion the radionuclides responsible for the highest radiation dose such as the lanthanides, ruthenium and zirconium are concentrated in form of an insoluble residue in the dissolver. This means that more than 95 % of the insoluble fission products can be contained in a shielded matrix.

Finally one recent improvement should be considered: The direct sublimation of molybdenum-(VI)-oxide from an adsorber matrix.

The sublimation step is an integral part of most Mo-separation processes because it guarantees that the product is not contaminated by organic impurities. The disadvantage of this procedure: It is labor intensive in operation and time consuming since the evaporation of the Mo-containing solution has to be carried out very carefully to prevent overboiling. These aspects initiated a research program to simplify this process. The basic idea was to find a suitable metal oxide which is able to adsorb the molybdenum quantitatively from aqueous solutions and which permits a thermal desorption of the molybdenum-(VI)-oxide by applying high temperatures /14/.

This research program was successful and an efficient system was developed based on the Mo-adsorption on SnO_2 and the subsequent thermal desorption of the molybdenum oxide in a H_2O -stream containing oxygen /15/. The total yield was found to be better than 97 % and the process time was reduced to one hour.

RECYCLING OF NUCLEAR FUEL

The insoluble residue in the dissolver contains about 99 % of the initially irradiated uranium in the form of uranium dioxide and alkaline diuranate together with the insoluble fission product species, above all ruthenium, zirconium, niobium, and the lanthanids. Under aspects of economy and safeguard regulations the nuclear fuel has to be recycled. The method presented here for this purpose is based on the formation of soluble negatively charged uranyl tricarbonato-complexes, a system industrially used

in uranium extraction from minerals /16/ and the fabrication of highly soluble U/Pu mixed oxides /17/. and investigated at the Institute of Radiochemistry, within the framework of the nuclear fuel reprocessing and waste treatment project /18-19/.

While dissolution in the presence of excess carbonate ions by complex formation of the diuranate proceeds quickly the dissolution of UO_2 calls for the presence of an oxidant such as oxygen or H_2O_2 /20/. The best results in dissolution are achieved by the use of hydrogen carbonate /carbonate mixtures. The uranium containing solution is contaminated with soluble carbonate species of the fission products, such as cerium, zirconium and niobium. Under these conditions ruthenium is highly susceptible to undergo hydrolysis so that only a minor fraction is carried into the carbonate solution.

The successful separation of the uranium from the fission products is accomplished by choosing conditions under which a fixation of the uranyl tricarbonate anions present in a high excess is avoided as far as possible, whereas the fission product carbonate species dissolved are retained on the column. In figure 8 the coefficients of the cerium, ruthenium, zirconium and niobium fission product distribution on carbonate loaded Bio-Rex 5, determined under static conditions, have been plotted for different carbonate concentrations in the aqueous phase /21/.

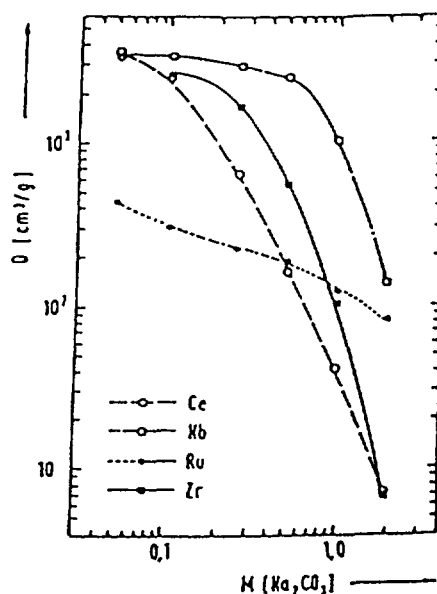


Fig. 8 Distribution coefficients of Ce-, Ru-, Zr- and Nb-carbonate species vs carbonate concentration.

Given the extremely small amount of fission product cations used in this experiment the carbonate concentrations plotted on the abscissa can be considered as the amount in excess of the stoichiometric amount required for complexing. It is evident from the

shape of the respective distribution curves that, except for ruthenium, a clear dependence exists of fission product retention on the excess of carbonate ions. However, the change of the fission product distribution coefficients as a function of carbonate concentration is here much smaller than in the uranyl carbonate system which is demonstrated by a comparison with figure 9 where the distribution coefficients of the uranyl carbonato-complex on the strongly basic exchangers AG1-X8, AG2-X8 and on the moderately basic exchanger Bio-Rex 5 are plotted as a function of the $U:CO_3^{--}$ ratio.

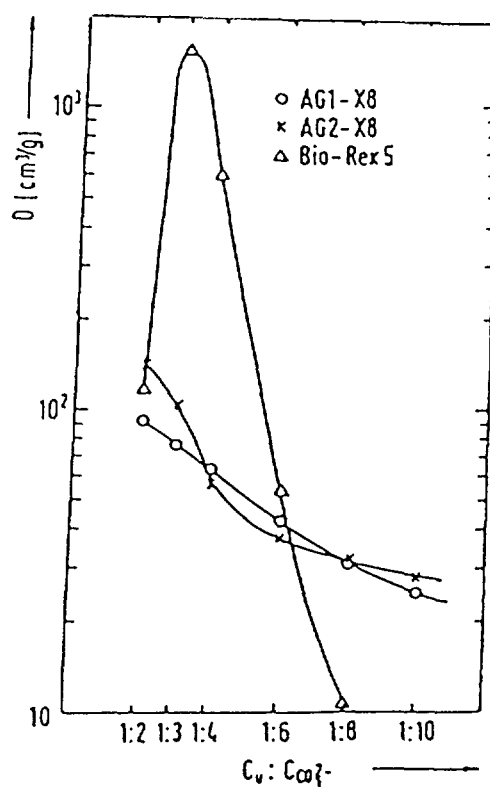


Fig. 9 Distribution coefficients of the uranium carbonato-complexes on AG1-X8, AG2-X8 and Bio-Rex 5 in carbonate solutions as a function of the UO_2^{++}/CO_3^{--} -ratio.

Thus the separation factors achievable under these conditions offer very favorable possibilities of separation of uranium which, with a sufficient hyperstoichiometric portion of carbonate, migrates through the column, whereas the majority of fission products are retained. Figure 10 shows the breakthrough curves of uranium and of the process relevant fission products cerium, ruthenium, zirconium, and niobium in carbonate medium determined under dynamic conditions.

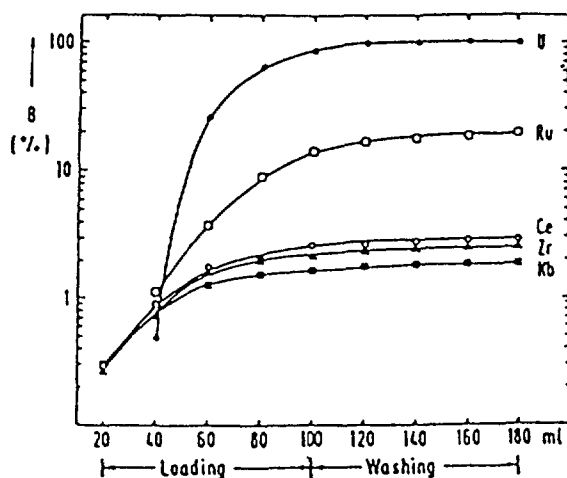


Fig. 10 Breakthrough in % of U, Ce, Ru, Zr and Nb in carbonate medium determined under dynamic conditions.

loading sol.	= 100 ml	column:
U-content	= 1.19 g	diameter = 15 mm
U:CO ₃ ²⁻ /HCO ₃ ⁻	= 1.7	length = 130 mm
90 % Na ₂ CO ₃ , 10 % NaHCO ₃		bed volume = 20 ml
washing sol.	= 0.2 M Na ₂ CO ₃	load. rate = 0.5 ml cm ⁻² min ⁻¹

It appears from this figure that cerium, zirconium and niobium are retained by more than 97 % in one run. Ruthenium forms species only very little soluble under these conditions so that a small part of it enters the process. About 80 % of it is retained on the exchanger. It is likewise evident from figure 10 that uranium, after washing of the column with four column volumes of a 0.2 M Na₂CO₃ solution is eluted almost without loss. The fission products can be eluted both with an Na₂CO₃ solution of higher concentration and with nitric acid; in case of acid elution the solution should be carried slowly from bottom to top of the column in order to avoid disturbances due to CO₂ released.

Under actual conditions the filtered solution was passed through a Bio-Rex 5 column conditioned with hydrogen carbonate. Generally 300 ml volume stainless steel columns were used. The diameter was 32 mm and the length 300 mm. The most favorable charging rates are 2 - 4 column volumes per hour. Experience in hot operation has been accumulated with 20 - 40 g uranium batches each. The mean decay times of the nuclear fuel were 4 - 8 weeks. The efficient decontamination process can best be visualized by the fact that the dose rate on the surface of the previously filtered process solution decreased on an average from 3000 - 4000 rad to about 100 rad after one passage through the column, measured at 20 cm distance [21/.

In the eluate containing the uranyltricarboxylate complex the $U:CO_3^{--}$ -ratio is reduced to about 3 or less and the resulting solution passed through a Bio-Rex 5 exchanger column. As shown in figure 10 at this ratio the uranium complex is retained on the column. Previous studies have demonstrated that Bio-Rex-5 is under these conditions superior to other exchangers such as AG1-X8 or AG2-X8 used by other authors.

Figure 11 shows the retention of uranium from carbonate solutions as a function of the amount of uranium absorbed (in g per kg resin).

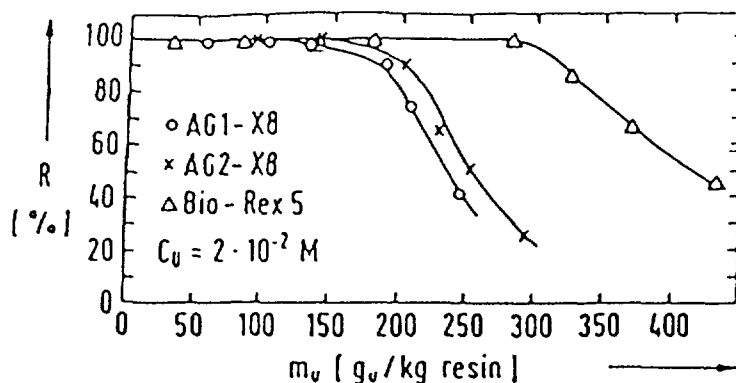


Fig. 11 Retention in % as a function of the amount of uranium absorbed in g per kg resin

It is evident from these results which were determined under static conditions that on Bio-Rex 5 more than 270 g uranium/kg exchanger are retained quantitatively while on AG1-X8 and AG2-X8 a maximum of 130 and 160 g uranium respectively, can be fixed until breakthrough occurs. The superiority of Bio-Rex 5 over the exchangers mentioned above is also evident if one considers that the elution with nitric acid can be accomplished with much smaller amounts of eluent (fig. 12).

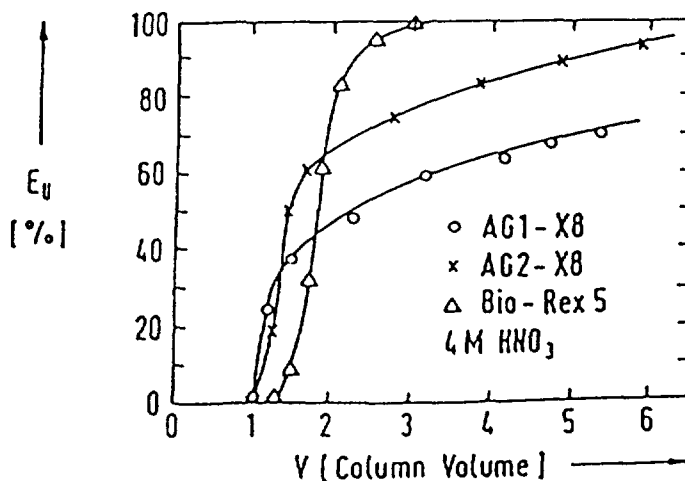
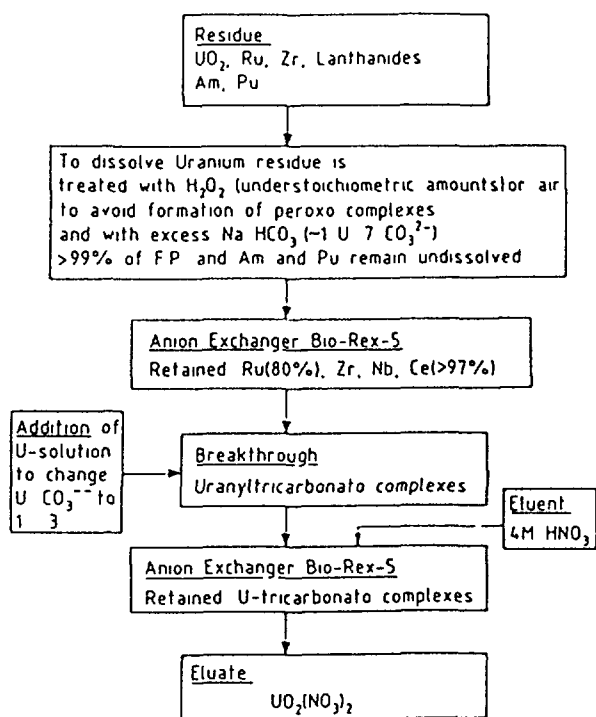


Fig. 12 Amount of uranium eluted in % vs volume of elution

Thus, in the Bio-Rex 5 system the uranium retained can be completely eluted with three column volumes of 4 M HNO_3 ; whereas comparable uranium elution yields on AG1-X8 and AG2-X8 columns, respectively, can be achieved only with much higher column volumes of eluent. The versatility of this system was also verified for decontamination of the basic carbonate containing process streams in nuclear fuel plants /22/.

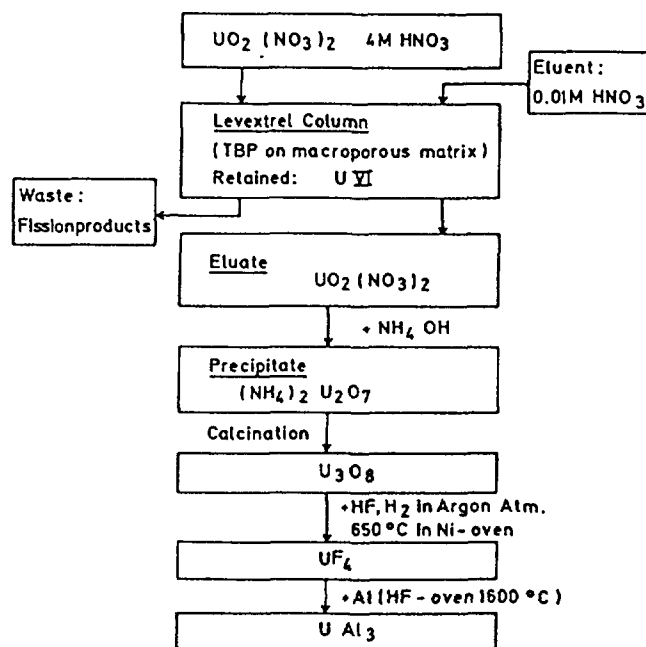
In figure 13 the flowsheet of the carbonate decontamination process is demonstrated.

The further purification of the uranium which is eluted with 4 M HNO_3 from the Bio-Rex 5 column is carried out by a chromatographic modification of the Purex process /23,24/. The purified uranium is precipitated with ammonia as ammonium diuranate. The dried ammonium diuranate is converted to U_3O_8 , subsequently to UF_4 and finally to UAl_3 . The powdered alloy is used for the production of target material by MTR-technique. Figure 14 presents the fuel decontamination process and the described process for UAl_3 -preparation.



Flowsheet of the basic nuclear fuel decontamination process

Fig. 13



Flowsheet of the TBP-solid bed purification system and the UAl_3 -alloy preparation

Fig. 14

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PRODUCTION OF FISSION ^{99}Mo BY PROCESSING IRRADIATED NATURAL URANIUM TARGETS

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Abstract

A production process for fission Mo-99 is proposed in which natural uranium as uranium oxide is used as target material. This procedure is particularly interesting for those which do not dispose of enriched nuclear fuel material. Approximately 400 g of uranium oxide enclosed in irradiation cans are dissolved in nitric acid after irradiation for 100 hrs at a neutron flux of $5 \cdot 10^{13} \text{ cm}^{-2} \text{ s}^{-1}$ in a research reactor. The separation of Mo-99 from the fuel-fission product solution is performed by ion exchange with alumina in a chromatographic column. Final purification includes the repeated chromatographic separation and subsequently a sublimation stage.

By this process about 100 Ci of Mo-99 is obtained at the end of the production process. The quality (radiochemical and radioactive purity) corresponds to international standards for medically used Mo-99/Tc-99m generators.

1. INTRODUCTION

Tc-99m labelled radiopharmaceuticals will probably be the most important radionuclide in nuclear medicine practice for the foreseeable future. In order to meet the requirements of modern diagnostic applications, a high radioactive concentration of the Tc-99m solution and therefore charging of the Mo-99/Tc-99m generators with Mo-99 of very high specific activity is indispensable. These results calls for versatile fission Mo-99 production processes in several countries. The separation of fission products from fuel-fission products solutions is tightly connected with problems such as management of high activities, also in volatile forms, multistage chemical separations under remote control and waste processing.

Most of the published procedures for the production of fission Mo-99 start from highly enriched uranium in form of special irradiation samples (1), (2), (3). This approach has the advantage of comparatively small processing units

and volumes as well as a small plutonium production. On the other hand, this highly enriched material is mostly available for such countries which dispose on a considerable national nuclear energy program. For the others, the availability of highly enriched uranium is already restricted and will certainly decrease in connection with the measures of the Non Proliferation Treaty.

For these reasons, a procedure is proposed which is based on the irradiation of natural uranium oxide and the well-known chromatographic separation according to the earlier Brookhaven process of Tucker et al. (4). The increased quality requirements since that time are considered by an additional purification step of Mo-99 sublimation. The layout of the proposed process relies on long lasting experiences in our laboratory where fission Mo-99 production in a 50 - 100 Ci scale was regularly under operation for years. It also considers the more stringent requirements in nuclear and radiation safety according to the contemporary international level.

2. DESCRIPTION OF THE PROCESS

The technological scheme is presented in Fig. 1. Main steps are the irradiation of the target, transport between reactor and processing unit, decanning, dissolution of the uranium oxide, treatment of gaseous effluents particularly the retention of radioiodine and radioxenon, separation and final purification of fission molybdenum and waste treatment.

- Irradiation

According to a representative example (400 g UO_2 in three cans of 20 mm diameter and 150 mm length at $5 \cdot 10^{13}$ n/cm² s for 100 h), 100 Ci Mo-99 is produced 48 h after the end of irradiation.

The total fission product radioactivity of the uranium oxide sample is shown in Fig. 2 in dependence of the decay time. At the beginning of processing this activity is mainly determined by radioactive isotopes of molybdenum, xenon, iodine and tellurium. On the other hand, for waste processing and storage $^{137}\text{Cs}/^{137\text{m}}\text{Ba}$ and $^{90}\text{Sr}/^{40}\text{Y}$ are most important.

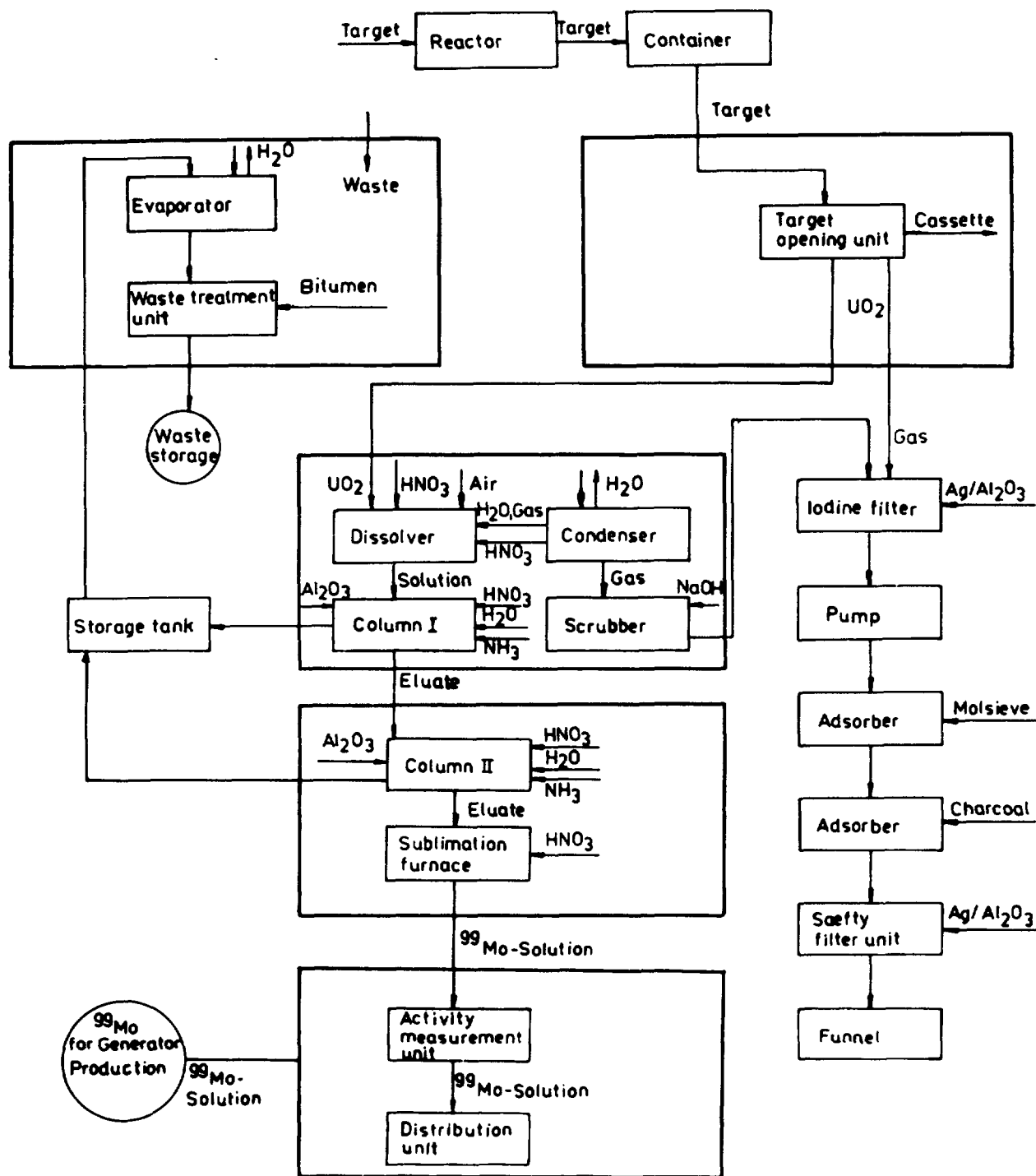


FIG.1. Technological flowsheet.

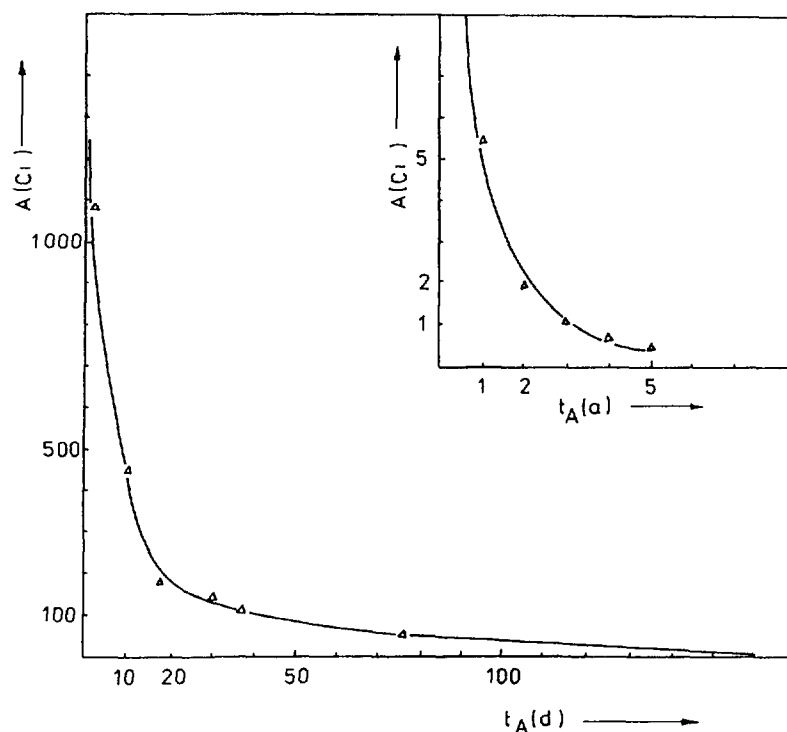


FIG.2. Radioactivity as a function of time.

Table 1 shows the activity of the production charge for several processing steps. The total activity decreases from 1086 Ci at the beginning to 54.6 Ci at the time of waste processing. The plutonium content is approximately 100 mg/batch. Plutonium accompanies uranium in the whole described process.

TABLE 1.

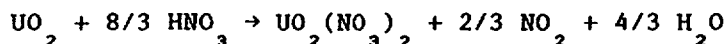
Activity of the several process steps		
time after irrd.	step	activity(Ci)
1 min	unloading cans	9916
24 h	transport to plant	1760
48 h	dissolution	1086
9 d	storage of process solution	447
76 d	waste processing	54
180 d	waste deposition	10
5 a	"	0.5

- Dissolution

After decanning, the irradiated uranium oxide is transferred into the dissolver. 700 ml of 6 N nitric acid, resulting in a final concentration of 500 mg/ml of uranium, is used. That means, the process proceeds under nitric acid depletion. The cristallisation temperature of such an acid

depletion uranium solution is 3 degrees centigrade. In comparison, a solution of the same uranium concentration, however, 1 N for nitric acid crystallises already at 18 degrees (5). Thus crystallisation of the dissolved $\text{UO}_2(\text{NO}_3)_2$ is excluded under the chosen conditions.

The stoichiometry of the dissolution follows the reaction equation



In addition, also some hydrogen and N_2O are present in the dissolver gas (~ 1 Vol%).

During the dissolution process air is continuously fed in the dissolver by an air lift in order to oxidize lower nitrous oxides to NO_2 and on the other hand to establish nitric acid circulation. In this process the main part of NO is washed out by the condensate in the reflux condenser. Addition of $\text{Hg}(\text{NO})_2$ to the feeding acid in a concentration of 1.10 mol/l allows the retention of the main part of radioiodine in the uranium-fission product solution. The process can be operated without molybdenum carrier, however, an addition of up to 100 mg Mo in form of $(\text{NH}_4)_2\text{MoO}_4$ does not influence the loading and elution of Mo-99/Tc-99m generators up to several 100 mCi per generator but greatly stabilises the total yield of the process.

After dissolution the final acid concentration is between 0.1 - 0.3 Mol/l, which is the optimal concentration range for adsorption on alumina from the uranium/fission product solution. The dissolution is completed after 2 hours. About 1% uranium remains undissolved under these conditions.

- Treatment of gaseous effluents

Radioiodine and xenon which escape during the decanning operation are removed by suction through an iodine absorption filter and a xenon delay line.

The iodine filters consist of alumina impregnated with silver nitrate. Decontamination factors of $>10^3$ for radioiodine have been observed under process conditions. The rare gas delay line consists of molecular sieve and charcoal filled absorbers at 30°C . Under process conditions the stay period is >50 days for xenon.

The reaction gases from the dissolution process pass a sodium hydroxide absorber before feeding in the iodine and xenon line. It is possible to establish a xenon separation for ^{133}Xe production by a bypass containing a charcoal filled absorber unit at 80°C which retains the necessary xenon activity.

Finally, the gas is fed into the cell ventilation after passing the xenon delay line. After passing usual radioiodine safety and particle filters these cell effluents are fed into the ventilation duct.

- Molybdenum Separation and Purification

The separation scheme follows the well-known Tucker process which does not need very special chemicals. The dependence of Mo-99 absorption on alumina as a function of uranium concentration is shown in Fig. 3. The process solution is diluted to an uranium concentration of 170-180 mg/ml by addition of washing solutions of the dissolver up to a total volume of 2 litres and then poured through an alumina column which contains 150-200 g alumina with a flow rate of about 10 ml/min.

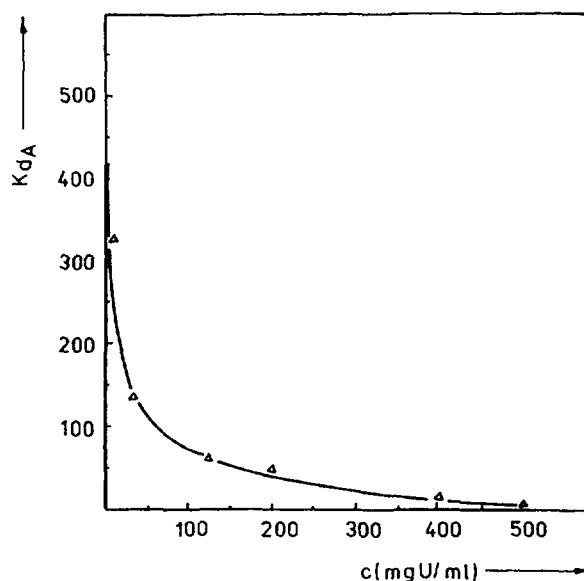


FIG.3. Distribution coefficient (K_{dA}) of ^{99}Mo as a function of uranium concentration.

By this procedure >95% of the Mo-99 activity is retained in the column. After washing with 150 ml 0.1 M HNO_3 , 150 ml H_2O and 0.01M NH_3 solution, the Mo-99 activity is eluted twice with 100 ml 1 M NH_3 . 90% of the Mo-99 activity is obtained in this way. The depleted dissolver solution containing uranium and the residual fission products are stored together until waste treatment.

Purification of the Mo-99 is accomplished by an additional chromatographic step followed by sublimation of the evaporated eluate. For this, the eluate is adjusted to 0.1 M HNO_3 and poured through a second small column filled with about 30 gm of alumina. After washing and elution the Mo-99 activity is in a volume of about 100 ml to which 10 ml of conc. HNO_3 is added and the mixture evaporated to dryness in three quartz ampoules. After heating the dry residue at 1000°C , the purified Mo-99 is dissolved in 50 ml 1 M NaOH and ready for loading Mo-99/Tc-99m generators.

- Waste Treatment

After storage for 80 days the liquid waste is evaporated in portions to dryness [400 g U as $\text{UO}_2(\text{NO}_3)_2$] directly in a stainless steel can. The alumina of the separation columns are also deposited in these cans. The cans, which represent the first containment, are put in a second can and sealed with bitumen. The activity is about 54 Ci/batch at the beginning of the waste treatment. The sealed cans will be given to the final waste storage.

3. PROCESS EQUIPMENT

The whole equipment of this technology is established in a line of 5 cells with the following tasks:

- C_1 : Waste Treatment
- C_2 : Entrance cell and decanning
- C_3 : Dissolution, gas purification and Mo-99 separation
- C_4 : Mo-99 purification
- C_5 : Activity measurement and confectioning.

Cells C_1 , C_2 , and C_3 are each equipped with one pair of master slave manipulators and shielded with lead bricks of 20 cm thickness. For manipulation in cells C_4 and C_5 , simple tongs are sufficient. These cells are shielded by a 15-cm lead (Table 2). The size of the cells 1000 x 1200 x 1300 cm corresponds to international standards. A conveyor system connects the cells of this line. The inactive process chemicals are fed through pipes from the operating corridor. All tubes with active fluids between the cells are located behind the shielding. Small process components and tools up to a weight of 5 kg can be introduced into the cells via the conveyor. The irradiated target is transported from the reactor to cell

TABLE 2.

Shielding data

cell	no.	process	activity	shielding dose (1 m)		working time	remarks
			C ₁	cm lead	mrem/h	h	
1(5)	waste proc.	150		20	1.55	40	for 0.5 mrem/h 22 cm Pb needed
2(1)	decanning	1100		20	14	2	for 5 mrem/h 22 cm Pb or 2 cm in- ternal local sh.
3(2)	dissolution	1100		20	14	8	for 0.5 mrem/h 26 cm Pb needed
	gas pur.Mo- separation						
4(3)	Mo-Purif.	110 Mo-99	10		0.5	8	
		10 I-132					
		5 I-131					
5(4)	Confect.	110 Mo-99	10		0.5	8	
	Storage	3000 FP	20				at full tank 50 % self shielding for 1500 C ₁ FP 20 cm Pb needed
	xenon delay	1000	20		0.5	8	
	safety filter	20	5		0.5		
2/3(1/2)	between cells		16		100		
3/4(2/3)	"		16		100		
4/5(3/4)	"		6		100		
5/1(4/5)	"		6		100		

C₂ in a specially adapted transport container and transferred into the cell through a port in the bottom. The canned waste is similarly extracted from cell C₁ by transfer in a special waste transport container. The Mo-99 solution is withdrawn also in a similar way from cell C₅ (Figs. 4.1, 4.2, 4.3, 4.4, 4.5).

The exhaust of all cells is connected and conducted through a radioiodine safety filter as well as a particle filter before feeding in the general ventilation system. The maintenance of the process equipment relies both on femo techniques e.g. valves, filter masses and direct intervention after decontamination (for long-living components constructed of stainless steel such as filter units, dissolver, etc.).

Waste Treatment Cell

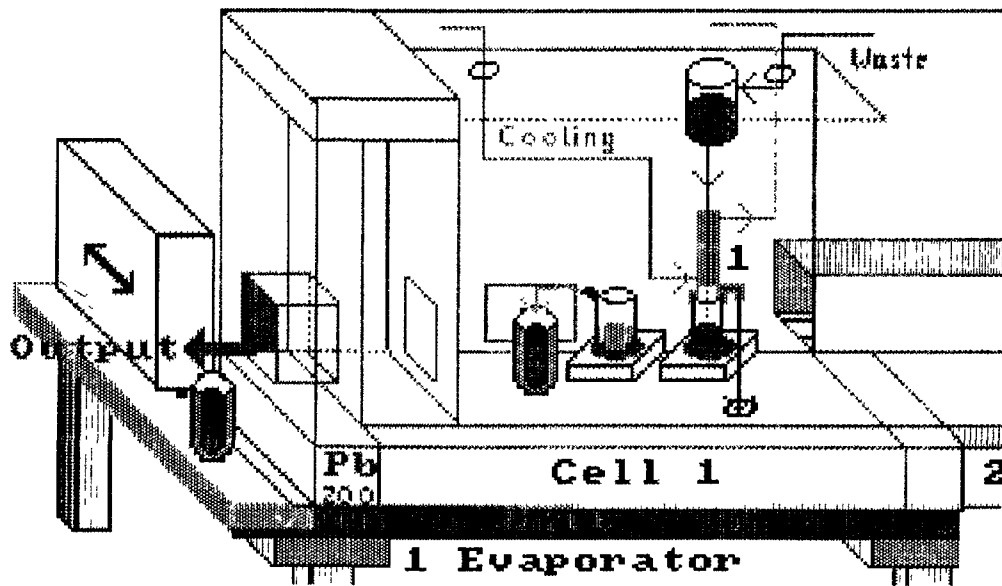


FIG.4.1. Arrangement of the apparatus in cell 1.

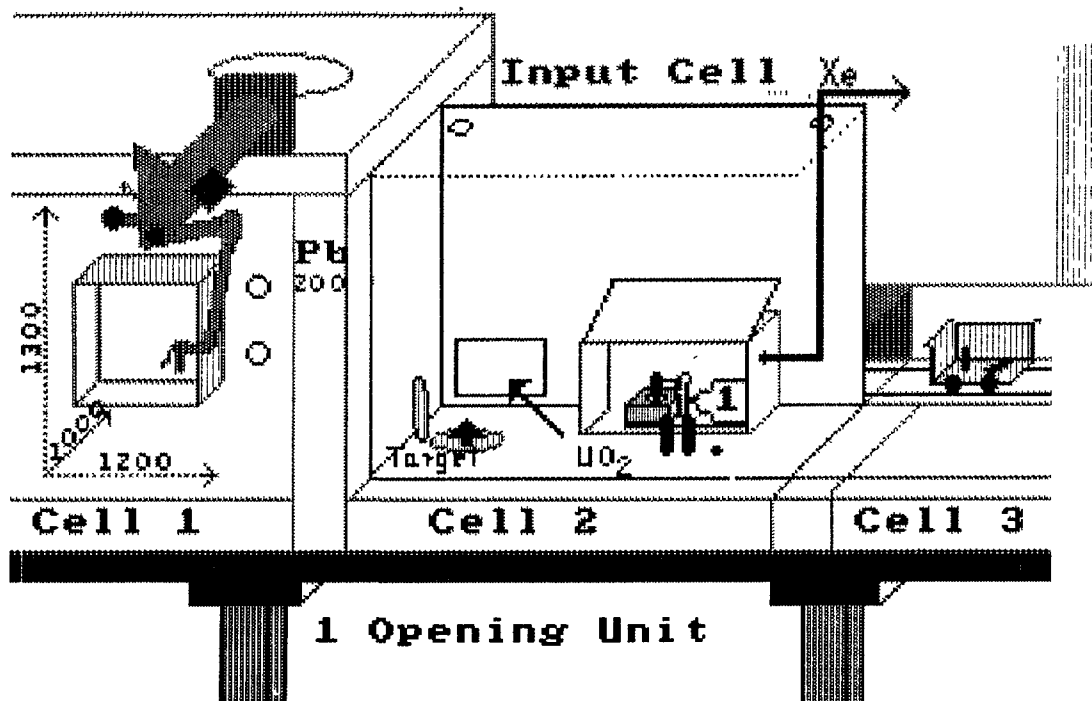


FIG.4.2. Arrangement of the apparatus in cell 2.

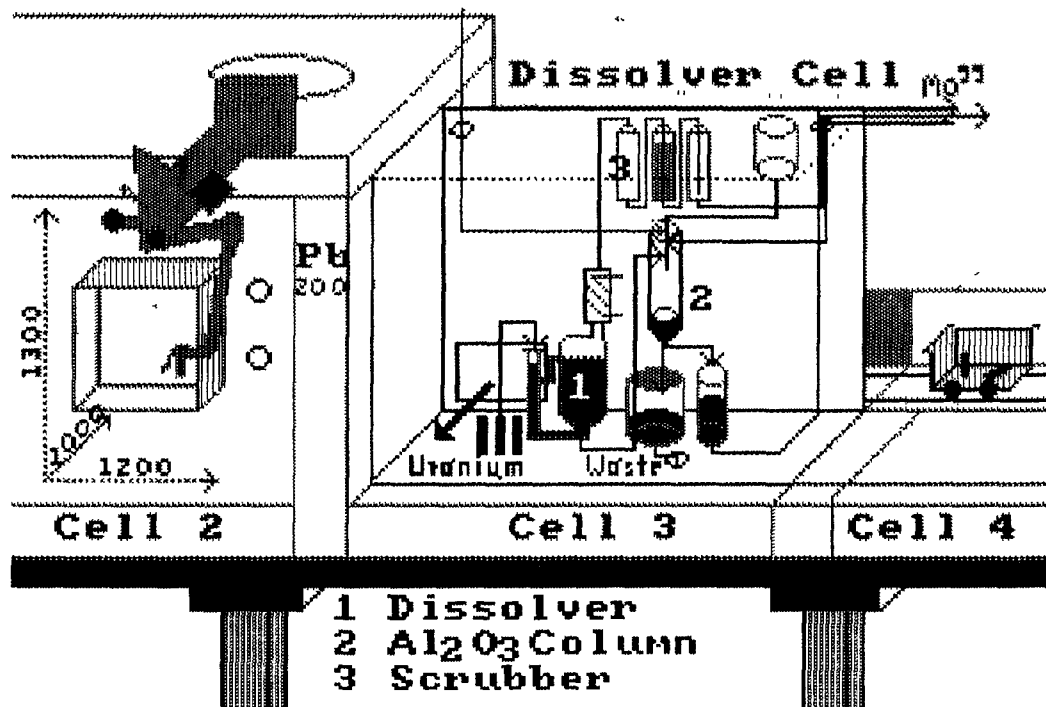


FIG.4.3. Arrangement of the apparatus in cell 3.

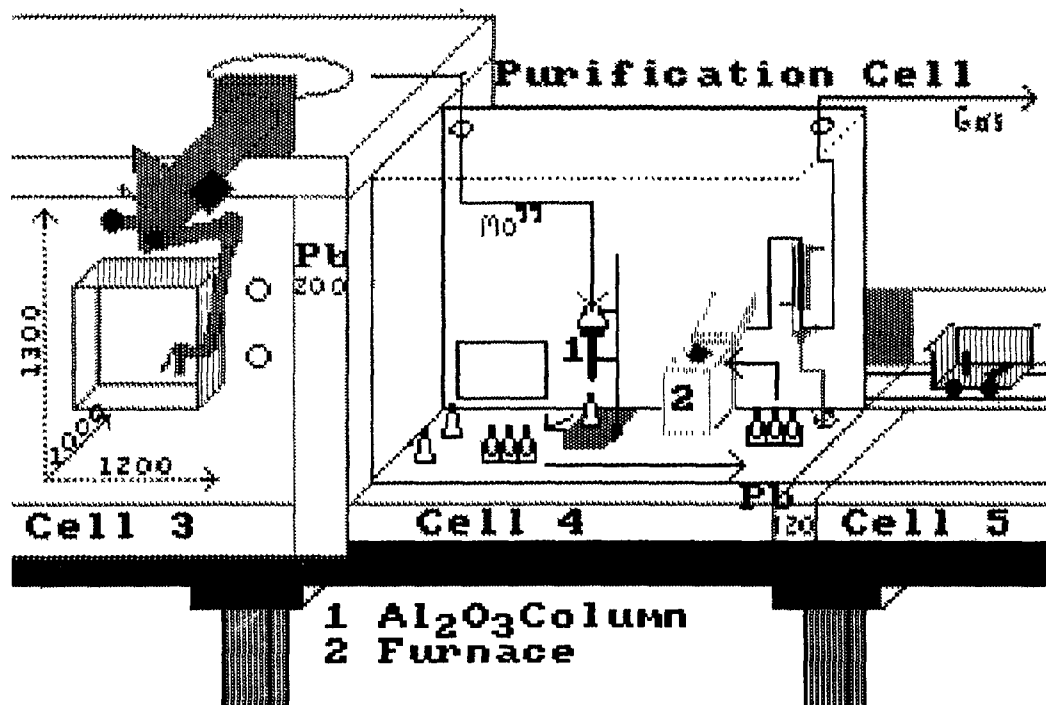


FIG.4.4. Arrangement of the apparatus in cell 4.

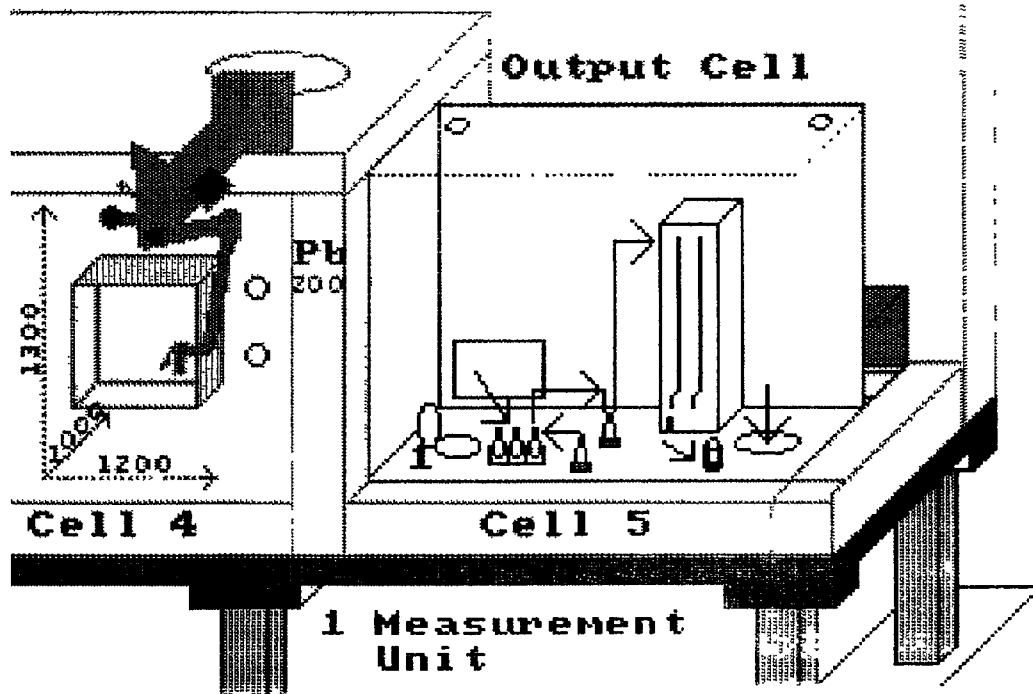


FIG.4.5. Arrangement of the apparatus in cell 5.

In Figs. 5.1, 5.2, 5.3, 5.4, 5.5, 5.6, and 5.7 the network of process tubes in cells C_1 through C_5 , in the gaseous effluent treatment system and the storage tanks, C_1 - C_5 , is depicted.

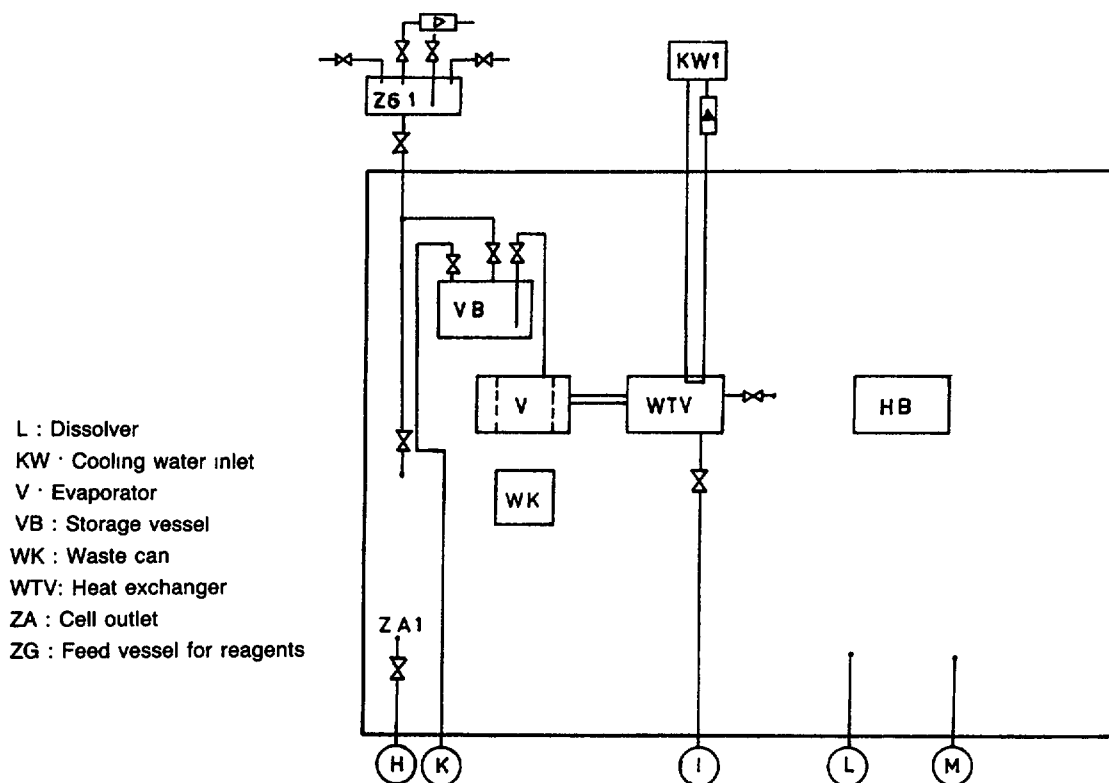


FIG.5.1. Pipe connections of cell 1.

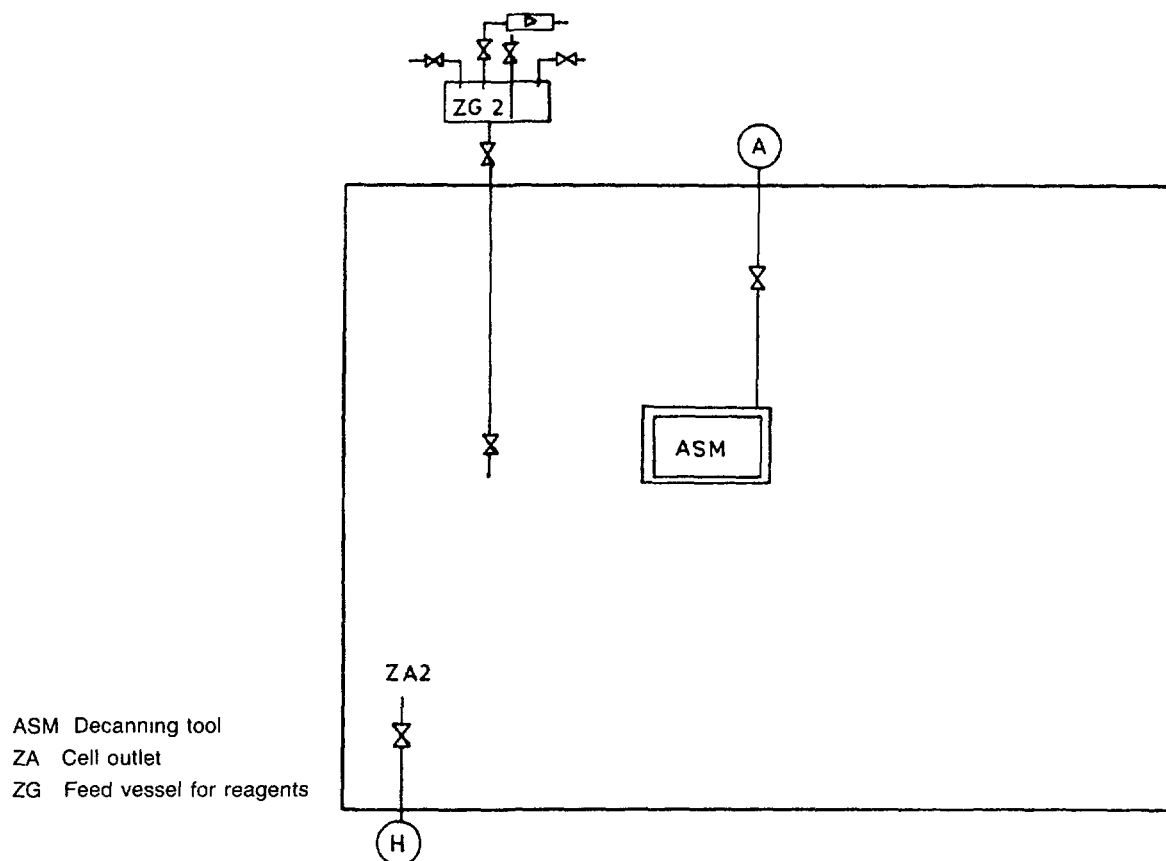


FIG 5.2 Pipe connections of cell 2.

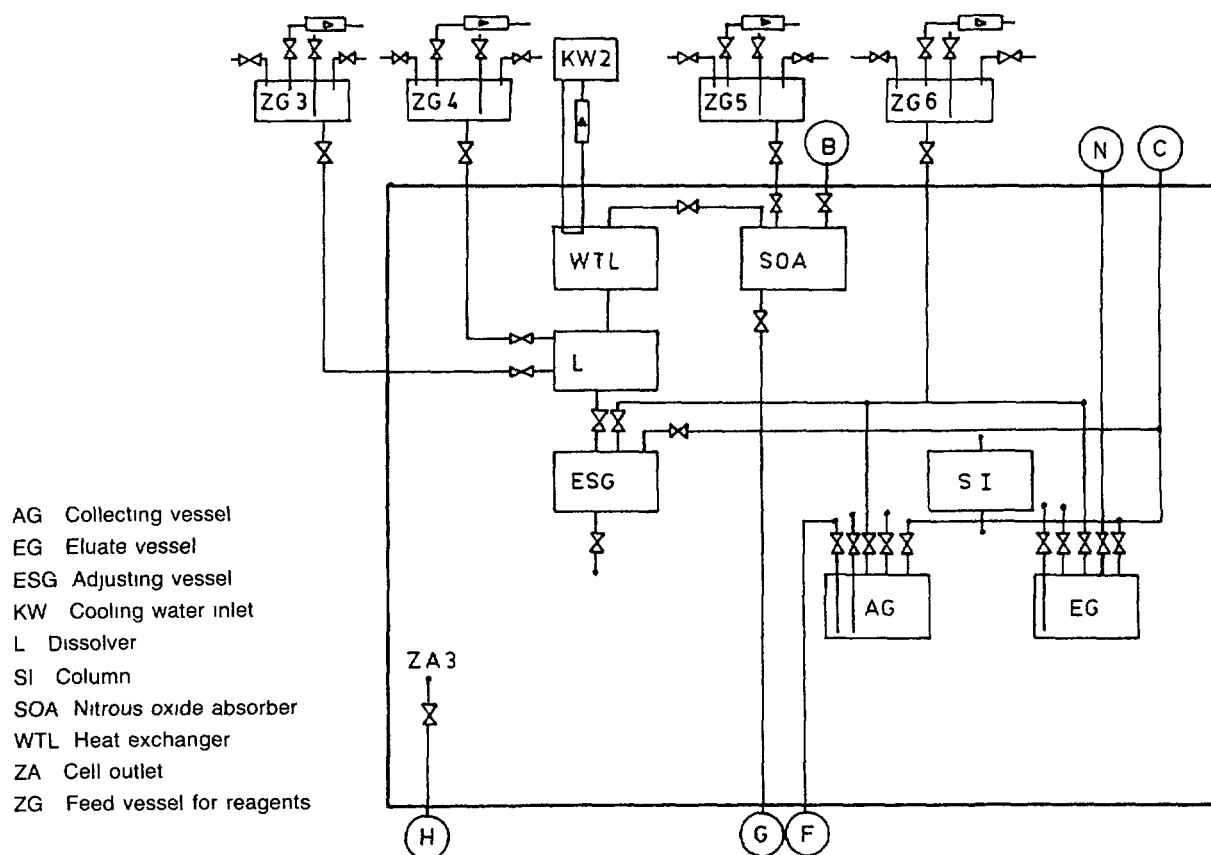


FIG.5 3. Pipe connections of cell 3.

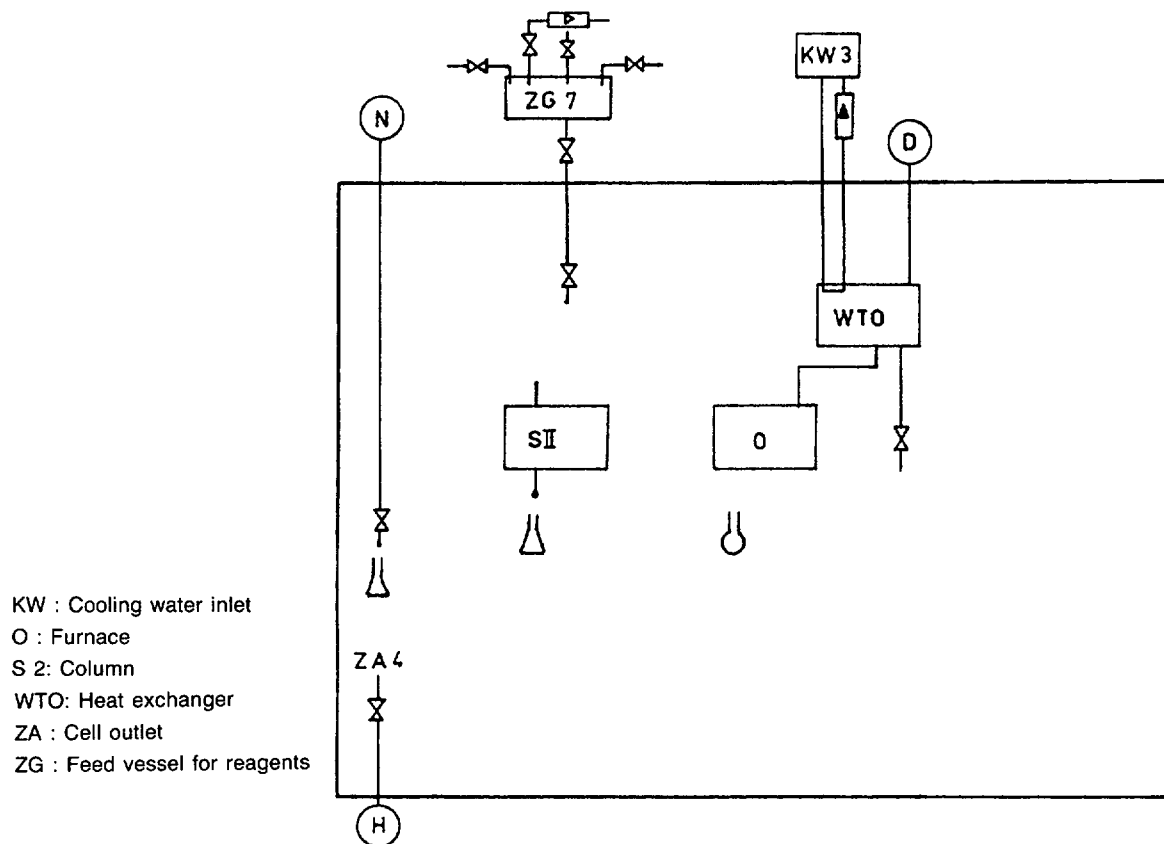


FIG.5.4. Pipe connections of cell 4.

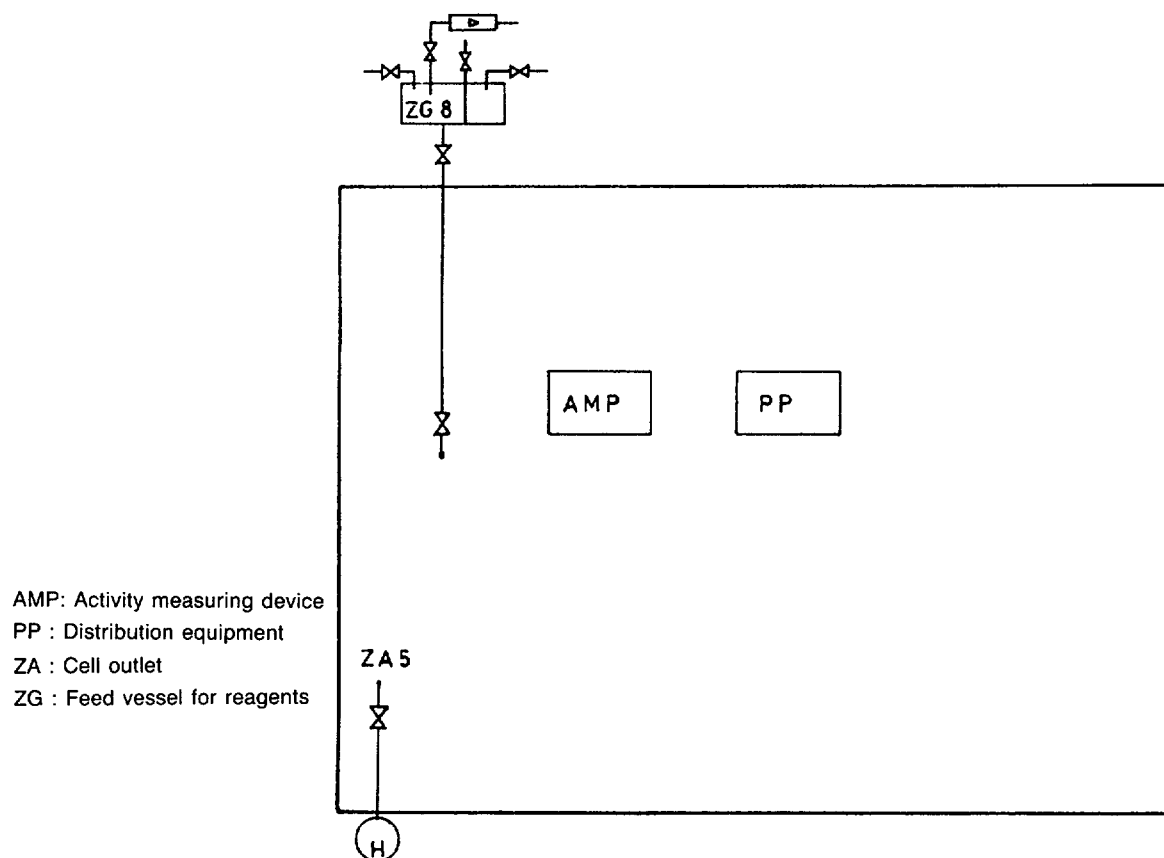


FIG.5.5. Pipe connections of cell 5.

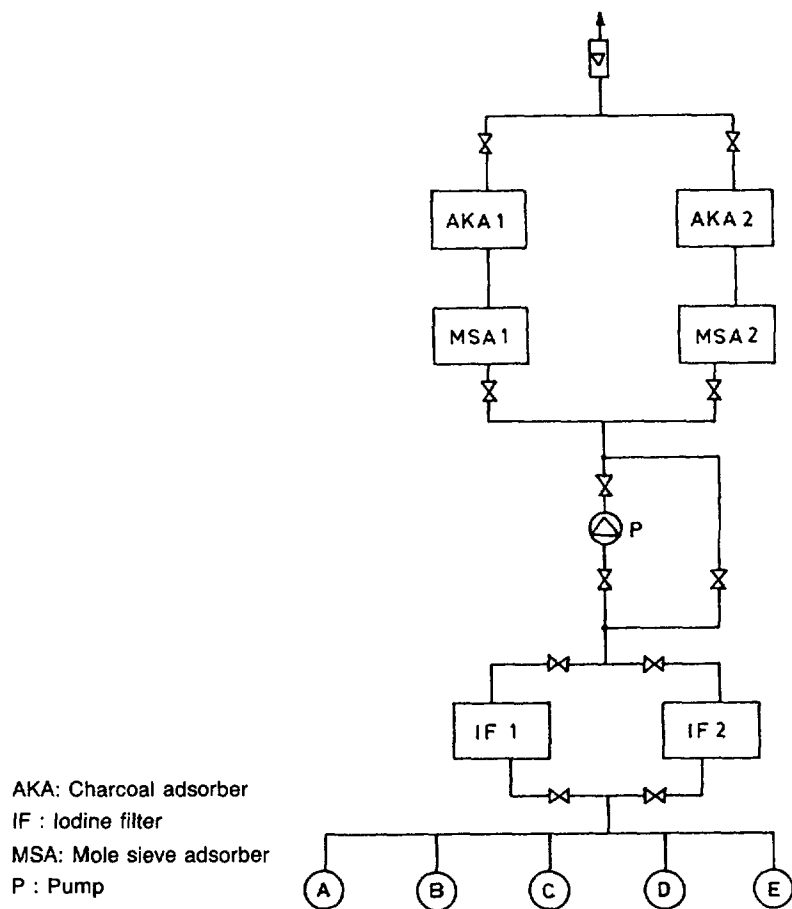


FIG.5.6. Schematic diagram of off-gas treatment.

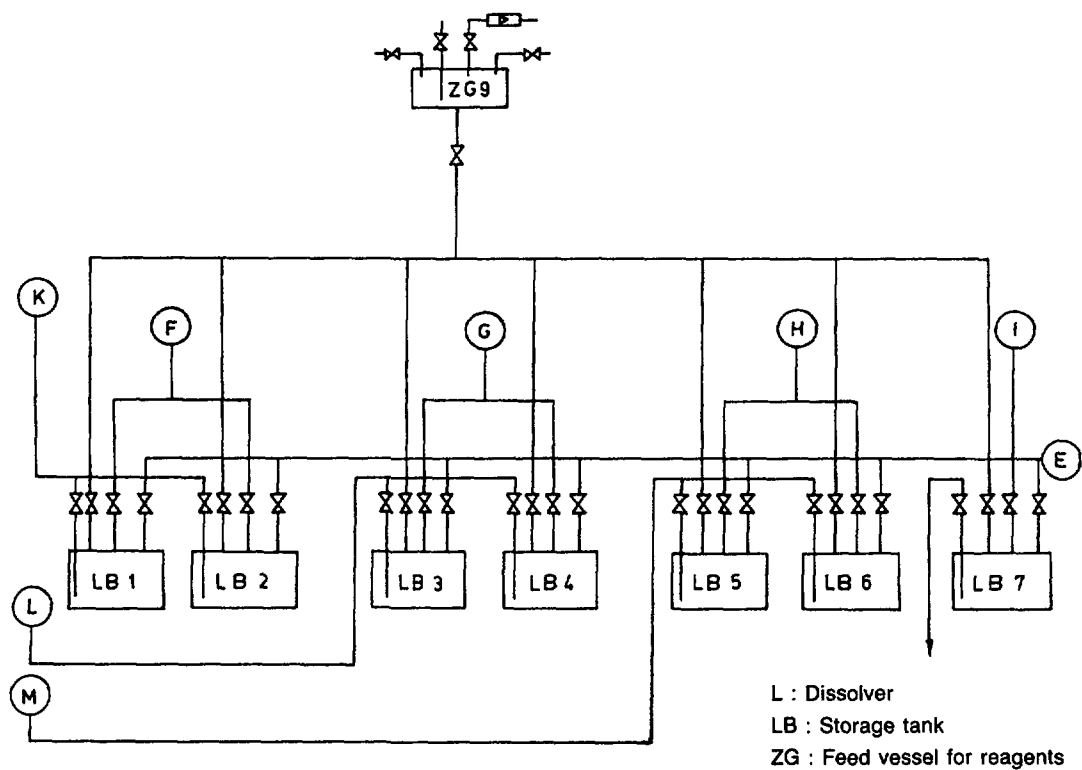


FIG.5.7. Schematic diagram of storage tanks.

4. PRODUCT SPECIFICATION

The total yield of the described technology is about 70% which in turn means that about 14 Ci of Mo-99 can be obtained with a precalibration date of 10 days. The working time is about 24 hours from the beginning (reception of the irradiated target) until delivery of the final Na MoO₄ solution. Two qualified technicians are necessary for running the process. Some quality parameters of the produced Mo-99 are given in Table 3. They correspond to the necessary quality required for generators used in nuclear medicine.

TABLE 3.

Quality parameters of the Mo-99 solution

spezific activity 3.7 .10¹⁰ Bq/g Mo
radiochemical purity Mo-99 as molybdate > 99 %
radionuclidic purity (ratio impurity/Mo-99 activity)

I-131	5.10	Zr-95	4.10
Ru-103	3.10	Sb-125	4.10
Ce-141	9.10	β-activity	4.10
Te-132/I-132	1.10	total alpha	10

The described process and technology was developed in our laboratory and experimentally verified with a view to have an alternative in case of complete breakdown of the large scale production plant, which would guarantee a domestical demand of about 50 generators per week. The process is very flexible with regard to the target material. Up to 80% enriched target material has been processed in the described way. In our opinion, this technology could be of interest for countries with a similar level of demand.

APPARATUS AND REAGENTS

Apparatus

Cells (1000x1200x1300 mm)
 box
 irradiation cans/batch
 transport container for irradiated cans
 decanning device
 dissolver
 reflux condenser
 NO - absorber
 column 1/batch
 column 2/batch
 furnace
 sublimation bulbs/batch
 Erlenmeyer flasks/batch
 adjusting vessel
 distribution(pipetting) device
 activity measuring device
 lead container for activity transport (Mo-99)
 storage tank
 evaporator
 waste cans/batch (stainless steel)
 iodine filter
 drying unit(mole sieve)
 adsorber (charcoal)
 freezer
 pump for reduced pressure
 iodine safety filter
 particle filter
 feed vessels
 pressure/reduced pressure unit
 tongs
 master slave manipulators
 lead glass windows
 lifting carrier
 lead for shielding
 flow meter
 pressure gauge
 activity measuring device (Xenon)
 titration device
 dosis meter (sphere ionisation chamber)
 activity alarm monitor
 reduced pressure gauge
 dosis meter (stationary)
 conveyor
 lifting carrier
 lifting device
 valves
 cooling water
 electrical energy
 cell illumination
 plugs (tubes,pipes,cables)

chemicals

400 gm UO_2 (0.7 % ^{235}U) /batch
 700 ml 6M HNO_3 /batch
 300 ml 0.1 M HNO_3 /batch
 200 mg Hg /batch
 10 l H_2O dest /batch
 300 mol HNO_3 1 M /batch
 200 mg Al_2O_3 /batch
 10 ml HNO_3 conc /batch
 100 ml M NaOH /batch
 3 l 5 M NaOH /batch
 50 kg Al_2O_3 impregnated with AgNO_3 /year
 50 kg charcoal / year
 50 kg mole sieve / year
 filter tissue 2 pieces /year

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RESEARCH AND DEVELOPMENT OF ^{99}Mo PRODUCTION TECHNOLOGY IN JAPAN

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Abstract

A fission ^{99}Mo plant was constructed in 1977 at the facilities of the Japan Atomic Energy Research Institute (JAERI). UO_2 pellets (2.6% enrichment) were utilized on target material containing 120 g of UO_2 . The pellets were irradiated in the JRR-2 and JRR-3 reactors up to 7 days at a neutron flux of 2 or $3 \times 10^{13} \text{ n/cm}^2 \times \text{sec}$. About 20 Ci of ^{99}Mo per week was routinely produced for 39 weeks. However, due to severe constraints of a research establishment, commercial production runs had been stopped. This paper provides information on the target configuration, post-irradiation separation process and waste disposal problems.

1. Introduction

Recently ^{99}Mo , the parent radionuclide of $^{99\text{m}}\text{Tc}$ used in nuclear medicine, is produced in large quantities. There are two nuclear reactions available for the production of ^{99}Mo using nuclear reactors; the $^{98}\text{Mo}(n, \gamma)^{99}\text{Mo}$ reaction and the nuclear fission of uranium. In the Japan Atomic Energy Research Institute (JAERI), the technology for ^{99}Mo production with both the neutron capture and the nuclear fission methods has been developed.¹⁾ In Table 1 are summarized the target materials, irradiation conditions, ^{99}Mo extraction processes, and specifications of products.

In JAERI, the ^{99}Mo production technology with the nuclear fission method using UO_2 (^{235}U 2.6%) pellets as a target material was established in 1977 and 740 GBq (20 Ci)

Table 1 Specifications for ^{99}Mo products of JAERI

	Neutron capture method	Fission method
Target material	MoO_3 pellets, 200 g	UO_2 pellets, 120 g (^{235}U 2.6%)
Irradiation		
Thermal neutron flux	$>10^{14} \text{ cm}^{-2}\text{s}^{-1}$	$2-3 \times 10^{13} \text{ cm}^{-2}\text{s}^{-1}$
Irradiation time	4-7 days	4-7 days
Cooling time	30 min	1-3 days
Irradiation vessel	Al	Stainless steel and Al duplicate
Extraction		
Radioactivities at processing	^{99}Mo 7.4 TBq (200 Ci)	F.P. 37 TBq (1000 Ci)
Facilities	Pb-cell (10-15 cm)	Heavy density concrete cave (80 cm)
Materials of apparatus	Quartz and glass	Stainless steel
Chemical processes	Dissolution in aq. NaOH	Dissolution in HNO_3 , extraction with D2EHPA and Al_2O_3 column chromatography
Processing time	2 h	24 h
Chemical yield	>99%	60-70%
Products		
Specific activity	$74 \text{ GBq}\cdot\text{g}^{-1}$ ($2 \text{ Ci}\cdot\text{g}^{-1}$)	$370 \text{ TBq}\cdot\text{g}^{-1}$ ($10000 \text{ Ci}\cdot\text{g}^{-1}$)
Radioactivity concentration	$19 \text{ GBq}\cdot\text{cm}^{-3}$ ($0.5 \text{ Ci}\cdot\text{cm}^{-3}$)	$37 \text{ GBq}\cdot\text{cm}^{-3}$ ($1 \text{ Ci}\cdot\text{cm}^{-3}$)
Chemical form	Na_2MoO_4 in NaOH (pH>7)	$(\text{NH}_4)_2\text{MoO}_4$ in 1 M NH_4OH
Radionuclidic	>99%	99%
Quantities of shipment	7.4 TBq (200 Ci)	740 GBq (20 Ci)
Major impurities	$^{92\text{m}}\text{Nb}$, $^{188\text{W}}$ - ^{188}Re	^{103}Ru , ^{131}I , ^{137}Cs , ^{141}Ce
Type of use	Solution type	Generator type

of ^{99}Mo was produced every week for 39 weeks a year. At present, however, all of the quantity of ^{99}Mo used in Japan is imported from overseas because JAERI cannot supply ^{99}Mo all year around without interruption. This is regrettable, but cannot be helped in an organization, where a limited number of nuclear reactors are used for research and development in all fields of atomic energy. Weekly production and supply of ^{99}Mo is indispensable for every day use of $^{99\text{m}}\text{Tc}$ in nuclear medicine.

In the course of research and development of ^{99}Mo production in JAERI, many technical achievements have been obtained, which include technologies to insert a target in and withdraw it from the reactor core regions during reactor operation for obtaining a product of high specific activities,

to treat unsealed fission products including ^{131}I in large quantities, and to process radioactive liquid wastes. This paper describes the outline of the ^{99}Mo production in JAERI.

2. Molybdenum-99 production with neutron capture and nuclear fission methods

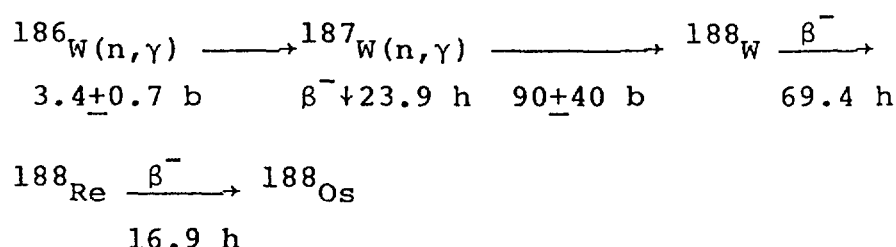
2.1 Neutron capture method

As a target material for ^{99}Mo production by the $^{98}\text{Mo}(n,\gamma)^{99}\text{Mo}$ reaction molybdenum trioxide (MoO_3) is usually used, and ^{99}Mo is obtained by dissolving the irradiated target in aqueous NaOH solution. For this method the radiation shielding is not so hard because the radionuclides produced in the target are only ^{99}Mo and $^{99\text{m}}\text{Tc}$. No serious radioactive waste is generated in the postirradiation processing. However, it is difficult to obtain a product of high specific activity because the thermal neutron cross section for the $^{98}\text{Mo}(n,\gamma)^{99}\text{Mo}$ reaction is as low as 0.13 b. Even if the MoO_3 target is irradiated, for example, for 8 days (approximately 3 time as long as the half-life of ^{99}Mo) in a nuclear reactor at the neutron flux of $1 \times 10^{14} \text{ cm}^{-2} \text{ s}^{-1}$, the specific activity of ^{99}Mo would be $37 \text{ GBq} \cdot \text{g}^{-1}$ ($1 \text{ Ci} \cdot \text{g}^{-1}$) or less. In this respect, the effective use of epithermal neutrons might lead to the production of ^{99}Mo with high specific activity because the epithermal neutron cross section for the $^{98}\text{Mo}(n,\gamma)^{99}\text{Mo}$ reaction is as high as 11.6 b.

Although ^{99}Mo produced by the neutron capture method has a demerit in preparing a small-size generator because of the limited specific activity, the following studies have been carried out to overcome this problem; (1) to enhance the specific activity by means of nuclear recoil effects,²⁻⁴⁾

(2) to prepare a ^{99m}Tc generator with molybdophosphate $\text{H}_4[\text{P}(\text{MoO}_7)_6]^{3-}$ instead of molybdate MoO_4^{2-} to increase the adsorption efficiency on alumina columns,⁵⁾ (3) to prepare alumina columns with a zirconium molybdate gel,^{6,7)} and (4) to produce ^{99}Mo from isotopically enriched targets with 91-99% of ^{98}Mo .⁸⁾

For ^{99}Mo production with the neutron capture method, it is of importance to reduce the amount of tungsten impurities in target materials because ^{188}Re is induced by the following reactions:



If a ^{99}Mo product contains ^{188}Re , it becomes hard to separate ^{188}Re impurities from ^{99m}Tc because the chemical property of Re is very similar to that of Tc.

2.2 Nuclear fission method

The thermal neutron fission yield of ^{235}U for ^{99}Mo is as large as 6.1%, and 740 GBq (20 Ci) of ^{99}Mo can be obtained from 1 g of ^{235}U irradiated in a nuclear reactor for 1 week at the thermal neutron flux of $1 \times 10^{13} \text{ cm}^{-2} \text{ s}^{-1}$. The specific activity would be higher than $370 \text{ TBq} \cdot \text{g}^{-1}$ ($10^4 \text{ Ci} \cdot \text{g}^{-1}$), which is practically regarded to be carrier-free. A ^{99}Mo product with high specific activity is advantageous for reducing the size and weight of generators, which facilitates the handling, transportation, and price.

The ^{99}Mo production with the fission method requires the extraction of ^{99}Mo in a very high purity from various fission products of which radioactivity is 20 times as high as that of ^{99}Mo itself. Although the processing scale would be relatively small, the process is essentially analogous to the nuclear fuel reprocessing. The ^{99}Mo production process would become much complicated because it is necessary to extract ^{99}Mo immediately after the neutron irradiation. Most of fission products become radioactive wastes, and the control and treatment are serious problems. The control of the volatile ^{131}I and ^{133}Xe as well as the radiation shielding for high energy γ rays from ^{140}La is a severe problem for the facility. Removal of hazardous radionuclides such as ^{90}Sr and ^{137}Cs makes the production process complicated. Nowadays, however, most of ^{99}Mo is produced with the fission method which does not necessarily require the use of high flux reactors. It is to be noted furthermore that ^{133}Xe obtained in the production process is a useful byproduct.

3. Molybdenum-99 production in Japan

3.1 Neutron capture method

In JAERI MoO_3 pellets (200 g) was irradiated for 4 to 7 days in a hollow cylindrical fuel (In-core hole) of the JRR-2 reactor operated at 10 MW. The thermal and epithermal neutron fluxes at the irradiation position were 1.3×10^{14} and $8.1 \times 10^{12} \text{ cm}^{-2} \text{ s}^{-1}$, respectively. The maximum specific activity of the ^{99}Mo product was $110 \text{ GBq} \cdot \text{g}^{-1}$ ($3 \text{ Ci} \cdot \text{g}^{-1}$) and 7.4 TBq (200 Ci) of ^{99}Mo was produced every week for 26 weeks a year.

The MoO_3 pellets (18 mm \varnothing x 18 mm) of which tungsten content was less than 30 ppm were enclosed in aluminum capsules and irradiated in heavy water of the In-core hole. The observed temperature of the target due to the γ heating was 243 °C at the center of the pellets and about 50 °C at the surface of capsules. These temperatures were low enough compared with the sublimation temperature of MoO_3 (\sim 750 °C). After the neutron irradiation the ^{99}Mo production was carried out using a cell with the lead shielding of 10 cm thick illustrated in Fig. 1. The lead shielding for a part of the cell where aluminum capsules were opened was thicker than the other part to protect γ rays of ^{24}Na induced by the $^{27}\text{Al}(n,\alpha)^{24}\text{Na}$ reaction. The pellets were transferred into a dissolution vessel made of quartz and then dissolved in aqueous NaOH solution. The whole processing was accomplished within 2 h. The specifications of the product are listed in Table 1 and the radioactive impurity nuclides contained in the product are listed in Table 2.

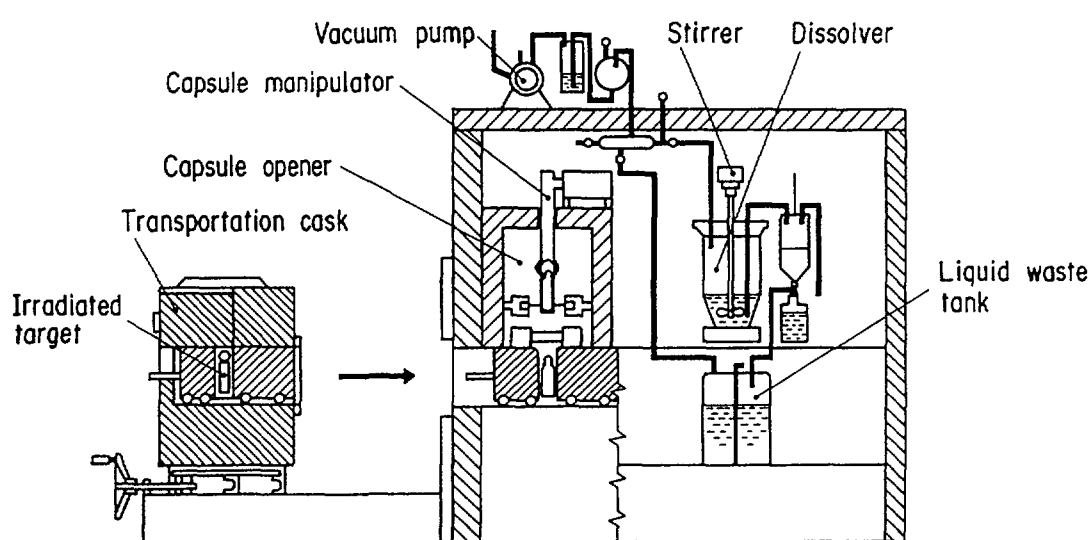


FIG.1. Facilities and apparatus for ^{99}Mo production from MoO_3 pellets by the neutron capture method.

Table 2 Radioactive impurities in ^{99}Mo products
from the neutron capture method

Radionuclidic impurities	Ratio to ^{99}Mo	Nuclear reactions
^{60}Co	8×10^{-6}	$^{59}\text{Co}(n, \gamma)$
^{65}Zn	3×10^{-7}	$^{64}\text{Zn}(n, \gamma)$
^{86}Rb	8×10^{-5}	$^{85}\text{Rb}(n, \gamma)$
$^{92\text{m}}\text{Nb}$	2×10^{-3}	$^{92}\text{Mo}(n, p)$
^{95}Nb	8×10^{-5}	$^{95}\text{Mo}(n, p)$
^{96}Nb	1×10^{-4}	$^{96}\text{Mo}(n, p)$
^{134}Cs	7×10^{-7}	$^{133}\text{Cs}(n, \gamma)$
^{99}Tc	3×10^{-10}	$^{99\text{m}}\text{Tc} +$
^{101}Mo	2×10^{-1}	$^{101}\text{Mo}(n, \gamma)$

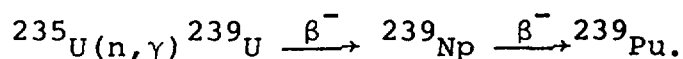
Values immediately after irradiation in the
in-core irradiation hole of JRR-2 for 7 days.

3.2 Fission method

(1) Reactor irradiation of ^{235}U

When 1 g of ^{235}U is irradiated with thermal neutrons at $1 \times 10^{13} \text{ cm}^{-2} \text{ s}^{-1}$ for 7 days, for example, approximately 740 GBq (20 Ci) of ^{99}Mo is produced, but about 500 W of heat is concurrently generated due to the nuclear fission. Therefore, it is of importance for safe irradiation not only to choose heat-resistant target and cladding materials, but also to remove the heat during the irradiation. From this point of view, U-Al alloys and UO_2 pellets are recommended as target materials.⁹⁻¹¹⁾ Although the melting point of U-Al alloys is not so high, the irradiation of the alloys with aluminum cladding immersed in the cooling water of nuclear reactors would be practical because of the high thermal conductivity of aluminum. It is also a favorable property for the postirradiation processing that U-Al alloys are easily dissolved in acidic and alkaline solutions.

Although the thermal conductivity is low and the temperature would become more than 1500 °C during the irradiation, UO_2 is an alternative target material because of its high melting point (2865 °C). Practically sintered UO_2 pellets with high density, of which thermal conductivity becomes higher than that of particles, enclosed in stainless steel or Zircalloy capsules is irradiated in nuclear reactors. The capsule plays a role as a first containment for gaseous fission products released from the target material at elevated temperatures. The outermost surface of capsules is eventually cooled with water stream during the irradiation. When UO_2 targets containing natural or low-enriched uranium are irradiated, it is to be noticed that the production rate of hazardous ^{239}Pu becomes higher by the reaction



In case of highly-enriched uranium, this problem is eliminated but it becomes harder to control the target temperature because of the extreme heat generation.

In JAERI UO_2 containing low-enriched uranium (^{235}U 2.6%) was chosen as a target material. Figure 2 shows the target assembly in which 120 g of UO_2 molded into 5 pellets (14.5 mm ϕ x 14 mm) was enclosed. The primary capsule was made of 304 stainless steel and the secondary one of aluminum. The gaps between the pellets, primary and secondary containers were 0.05 mm. Helium was filled in the plenum inside the capsule. The secondary capsule was provided with fins to enhance the cooling efficiency with water. With this type of capsules UO_2 pellets were irradiated with thermal neutrons in JRR-2 and JRR-3 reactors for 4 to 7 days at $2\text{--}3 \times 10^{13} \text{ cm}^{-2} \text{ s}^{-1}$.

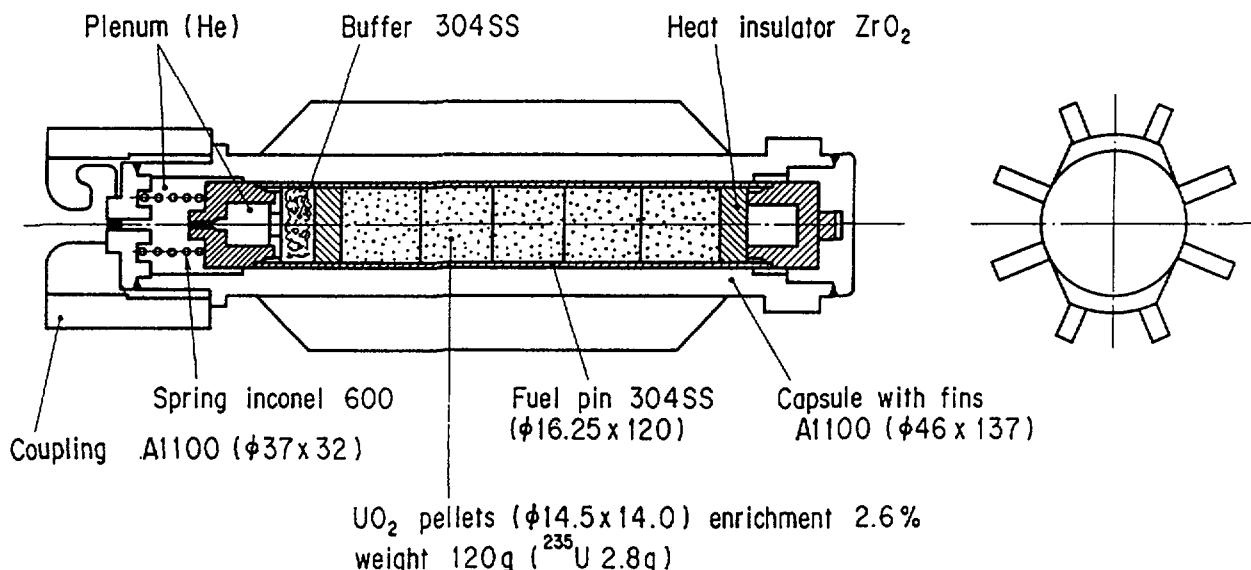


FIG.2. A UO₂ target for ⁹⁹Mo production by the fission method.

(2) Postirradiation processing

In neutron-irradiated UO₂ targets large amounts of fission products are contained. After two-day cooling, for example, 56 TBq (1500 Ci) of total fission products is contained in addition to 2.8 TBq (76 Ci) of ⁹⁹Mo; i.e., 4.1 TBq (110 Ci) of ¹³¹I, 2.6 TBq (70 Ci) of rare gases including ¹³³Xe, and 1.5 TBq (40 Ci) of ¹⁴⁰La. It is therefore necessary to install the extraction apparatus in an airtight cell or cave with heavy shielding.

In JAERI the neutron-irradiated UO₂ pellets were dissolved in nitric acid solution and ⁹⁹Mo was extracted with D2EHPA. The ⁹⁹Mo was then purified by means of alumina column chromatography. The whole process is schematically shown in Fig. 3.

When irradiated capsules is opened, radioactive iodine and rare gases stored in the plenum inside are released. These gases are removed in an evacuated reservoir and stored there.

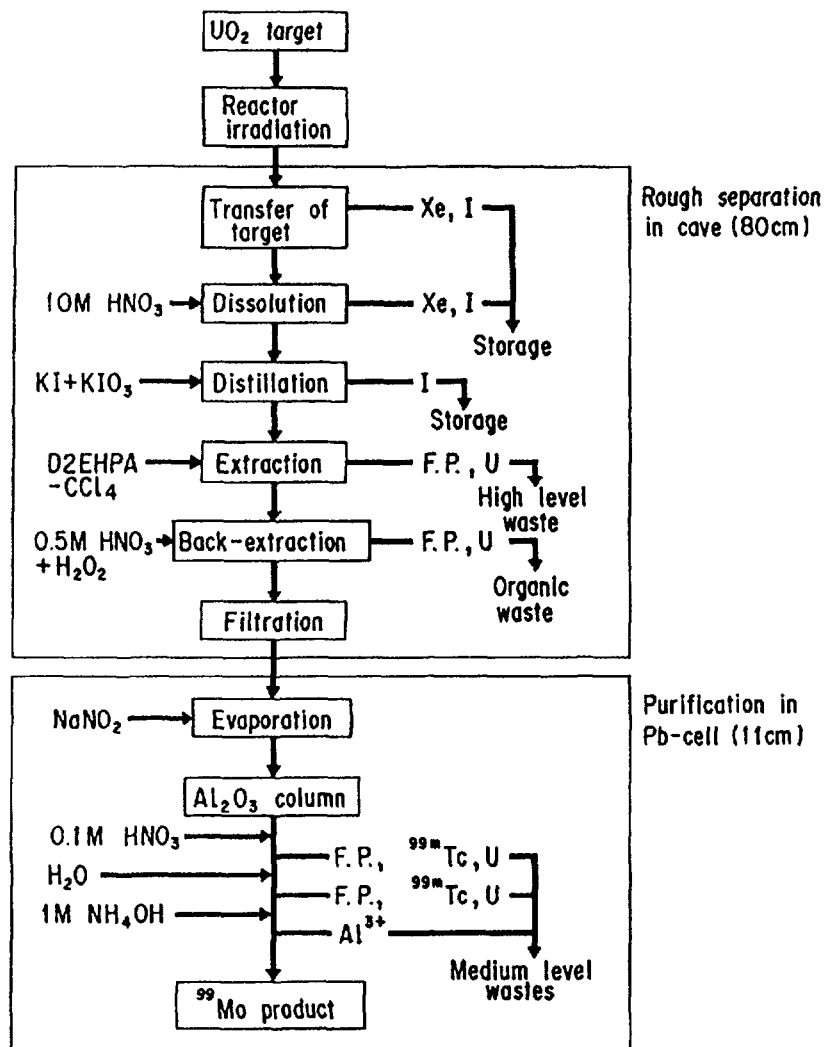


FIG.3. Flow diagram of the ⁹⁹Mo extraction process.

The UO_2 pellets are transferred into a dissolution vessel. When the UO_2 pellets are dissolved in 10 M HNO_3 solution, some portions of radioactive gases are evolved. These gases are introduced to alkali scrubbers connected to the dissolution vessel to collect ^{131}I and then transferred through pipings from the cave into molecular sieve columns, placed in the cell, cooled with liquid nitrogen to collect ^{133}Xe .

After distillation of the UO_2 -dissolved solution in which iodine carrier is added to remove ^{131}I , ⁹⁹Mo is extracted in the organic phase by stirring with D2EHPA

solution. Almost all of the fission products are retained in the aqueous phase and stored in a tank for high-level wastes.

The ^{99}Mo is back-extracted in aqueous solution with 0.5 M HNO_3 solution containing H_2O_2 . The organic solution containing trace amounts of uranium and fission products is stored in a tank for organic wastes. The processing described above is performed with the apparatus installed in the cave with heavy-density concrete shielding of 80 cm thick.

The aqueous solution containing ^{99}Mo is transferred into the cell with lead shielding of 11 cm thick. After decomposition of H_2O_2 with NaNO_2 , the volume of aqueous solution is reduced by evaporation and then the solution is passed through a column filled with alumina on which ^{99}Mo is adsorbed. The column being washed with 0.1 M HNO_3 and water, ^{99}Mo is eventually eluted with 1 M NH_4OH solution.

Figure 4 illustrates a conceptual drawing of the apparatus used for ^{99}Mo extraction from neutron-irradiated UO_2 pellets. The apparatus was made of stainless steel and consists of several units such as the dissolution—distillation, extraction—back-extraction, and exhaust gas processing, which are individually equipped in stainless steel boxes. In case of maintenance and repair, each unit can be replaced. The piping and wiring for the unit are coupled and decoupled by remote operation. Solenoid valves are used for the addition of reagents and transfer of liquid materials.

Processing of radioactive gaseous wastes is a serious problem in the ^{99}Mo extraction from fission products. Although most of ^{131}I and ^{133}Xe are recovered in the above mentioned

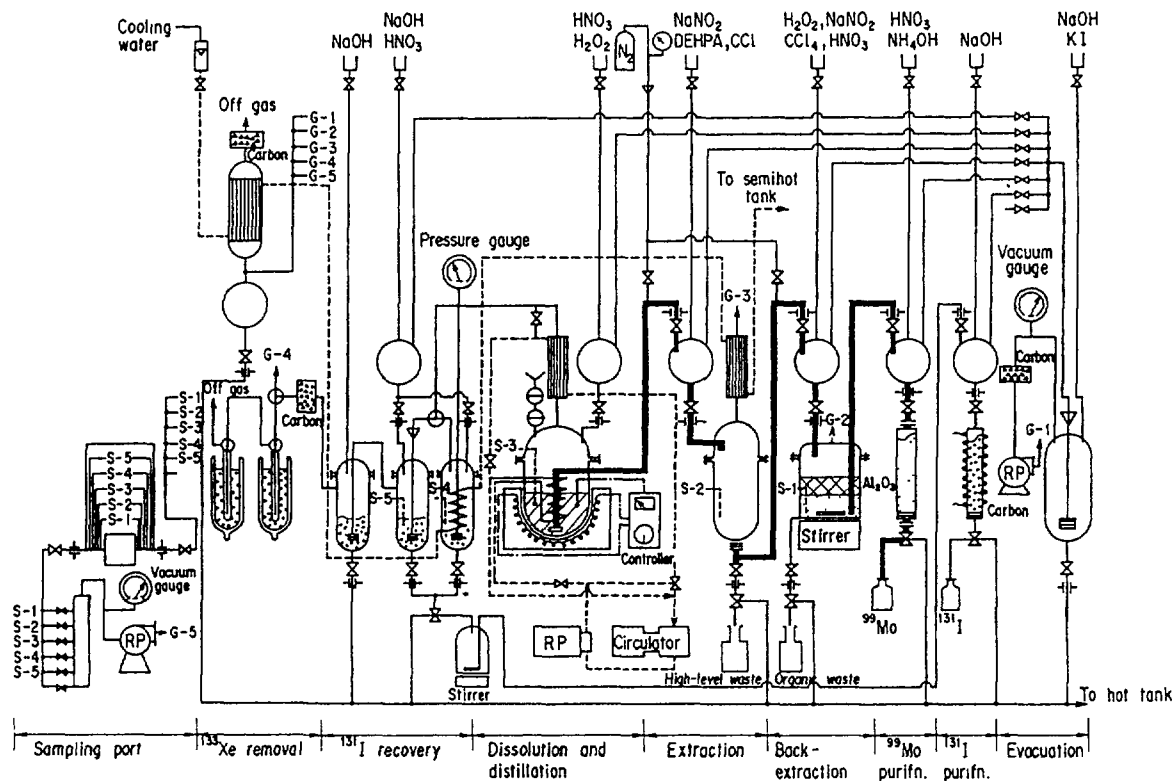


FIG.4. Conceptual drawing of apparatus for ^{99}Mo extraction from UO_2 pellets.

Table 3 Radioactive impurities in ^{99}Mo products from the fission method

Radionuclidic impurities	Half-life	Ratio to ^{99}Mo
^{131}I	8.05 d	1×10^{-5}
^{103}Ru	39.5 d	5×10^{-7}
^{95}Nb	35.0 d	2×10^{-6}
^{141}Ce	32.5 d	1×10^{-7}
^{89}Sr	52.7 d	$<6 \times 10^{-6}$
^{91}Y	58.8 d	$<9 \times 10^{-8}$
^{95}Zr	65.5 d	$<5 \times 10^{-9}$
^{132}Te	77.7 h	$<1 \times 10^{-4}$
^{137}Cs	30.0 y	$<3 \times 10^{-9}$
^{140}Ba	12.8 d	$<2 \times 10^{-7}$
^{239}Np	2.346 d	$<2 \times 10^{-3}$

Values 7 days after irradiation for 7 days.

process, a small portion of organic iodides such as methyl iodide contained in the atmosphere inside the cave would be released in the exhaust system of the facility. Hence, activated-carbon filters were furnished in the exhaust system.

The specifications of the product are listed in Table 1 and the radioactive impurities determined for the product are listed in Table 3.

(3) Processing of radioactive liquid wastes

Separation of dominant radionuclides contained in liquid wastes generated from ^{99}Mo production processes would be valuable in aspects not only of reduction of the waste volume, but also of development of a waste processing technology. The JAERI's experience is described in this section.

In high-level liquid wastes, 1.1 kBq cm^{-3} ($0.03 \text{ }\mu\text{Ci cm}^{-3}$) of α emitters such as U and Pu and 1.7 MBq cm^{-3} ($74 \text{ }\mu\text{Ci cm}^{-3}$) of fission products such as ^{90}Sr , ^{106}Ru , ^{137}Cs , and ^{144}Ce were contained in 130 L of nitric acid solution. Uranium was precipitated as sodium biuranate by neutralization. Strontium-90 was adsorbed on granular α -titanic acid. Ruthenium-106 was adsorbed on a composite adsorbent of zinc and activated carbons. Caesium-137 was coprecipitated with nickel hexacyanoferrate(III). The decontamination factor was more than 10^4 for each nuclides.¹²⁾

The medium-level liquid waste (520 L) containing a small amount of uranium and 6.7 kBq cm^{-3} ($0.18 \text{ }\mu\text{Ci cm}^{-3}$) of ^{90}Sr , ^{106}Ru , ^{137}Cs , and ^{144}Ce was processed as follows. Uranium and ^{144}Ce were coprecipitated with aluminum hydroxide using an electrolytic floating method. The filtrate was passed

through columns of zeolite, α -titanic acid, and a composite adsorbent of zinc and activated-carbon successively to remove ^{137}Cs , ^{90}Sr , and ^{106}Ru , respectively. The decontamination factor of ^{144}Ce was 10^5 and that for the other nuclides was 10^3 .¹³⁾

The organic liquid waste (90 L) containing 7.4 kBq cm^{-3} ($0.2 \text{ }\mu\text{Ci cm}^{-3}$) of α emitters such as uranium and 16 MBq cm^{-3} ($430 \text{ }\mu\text{Ci cm}^{-3}$) of fission products such as ^{95}Zr was processed with sodium carbonate solution; i.e., a stripping method or the DAPEX method in the refining of uranium. Ethanol was added to the solution to enhance the phase separation, and nearly 10^3 of the decontamination factor was obtained for each component. Uranium was precipitated as calcium biuranate from the aqueous phase. The organic phase was evaporated to separate carbon tetrachloride and D2EHPA.¹⁴⁾

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PRELIMINARY INVESTIGATIONS FOR TECHNOLOGY ASSESSMENT OF ^{99}Mo PRODUCTION FROM LEU TARGETS*

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Abstract

This paper presents the results of preliminary studies on the effects of substituting low enriched uranium (LEU) for highly enriched uranium (HEU) in targets for the production of fission product ^{99}Mo . Issues that are addressed include (1) purity and yield of the $^{99}\text{Mo}/^{99\text{m}}\text{Tc}$ product, (2) fabrication of LEU targets and related concerns, and (3) disposal of radioactive waste. Laboratory experimentation was part of the efforts for issues (1) and (2); thus far, radioactive waste disposal has only been addressed in a paper study. Although the reported results are still preliminary, there is reason to be optimistic about the feasibility of utilizing LEU targets for ^{99}Mo production.

INTRODUCTION

Technetium-99m for medical purposes is a decay product of ^{99}Mo , which is produced in research reactors from the fissioning of ^{235}U or from neutron capture of ^{98}Mo . This effort is related only to fission-product ^{99}Mo . Presently, ^{99}Mo is produced from a variety of target designs that contain HEU (93% ^{235}U). These designs include curved fuel plates,^{1,2} fuel rods,³ and cylinders with a film of UO_2 electroplated on the inside surface.^{4,5}

The overall purpose of this study is to assess the feasibility of substituting LEU for HEU in targets for production of fission-product ^{99}Mo . The main issues that were addressed are (1) purity and yield of the $^{99}\text{Mo}/^{99\text{m}}\text{Tc}$ product, (2) fabrication of LEU targets and related concerns, and (3) disposal of radioactive waste. Important issues yet to be addressed are the overall safety and economics of irradiating and processing LEU targets. This paper reports on the present status of our investigations.

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Preliminary experiments have been performed to study the effect of using LEU on Mo yield and purity during the separation of Mo from acidic target-dissolver solutions. Our experiments to date have been performed using stable Mo, depleted U, ^{239}Pu , ^{237}Np , and three fission-product radioisotopes ($^{110\text{m}}\text{Ag}$, ^{131}I , and ^{137}Cs). We have also studied the feasibility of electrodepositing U metal onto a stainless steel substrate for fabrication of LEU targets.

PURIFICATION OF ^{99}Mo FROM SIMULATED LEU TARGETS

Two methods of separating Mo have been studied thus far: (1) α -benzoinoxime precipitation (α -BP) of Mo and (2) adsorption of Mo by Ag-coated activated charcoal (ACAC). All separations were performed from acidic solutions, typical of that produced from the dissolution of UO_2 films. Table 1 compares reference HEU and LEU targets for ^{99}Mo production. The fissile content of the reference LEU target was adjusted to have the same fission reaction rate in an LEU-fueled core as the HEU target in a HEU-fueled core. The change in target material from HEU to LEU will affect the separation by increasing the amount of uranium to be dissolved and separated from ^{99}Mo by a factor of ~ 6 and increasing the amount of alpha-emitting isotopes and ^{239}Pu in the irradiated target by factors of 13 and 26, respectively.

Table 1. Reference HEU and LEU Targets for ^{99}Mo Production

	HEU	LEU ^a
^{235}U enrichment, %	93	19.75
^{235}U , g	15	18.5
Total U, g	16.1	93.7
^{99}Mo yield, ^b Ci (mg)	532 (1.11)	545 (1.13)
Total Mo, ^c (mg)	- (9.8)	- (10.0)
^{239}Np ^b (mg)	- (0.14)	- (3.8)
^{239}Pu , ^d μCi (mg)	28 (0.44)	722 (11.8)
Total α produced, ^d μCi	62 ^e	793 ^f

^aIn the calculations, the LEU target was produced in an LEU-fueled reactor.

^bAt the time it leaves the reactor core.

^cIncludes stable Mo isotopes and ^{99}Mo at time it leaves the reactor core.

^dAssuming all ^{239}Np ($t_{1/2} = 2.35$ d) has converted to ^{239}Pu ($t_{1/2} = 2.44 \times 10^4$ y).

^eIncludes 34 μCi due to U isotopes.

^fIncludes 66 μCi due to U isotopes.

These initial studies compared the effectiveness of separating ^{99}Mo from U, Pu, Np, and fission products under conditions of higher concentrations of U and/or volumes of dissolver solution.

Technetium generators contain sufficient ^{99}Mo (as molybdate on an acidic alumina support) to elute up to several Ci of $^{99\text{m}}\text{Tc}$ in 5 mL volumes on a daily basis. Radioisotope impurities in the eluate are of great concern, and several studies have examined this problem.⁶⁻¹⁵ The most stringent conditions cited in these studies for γ - and β -emitters is that they should be kept below $0.1 \mu\text{Ci/mCi}$ of $^{99\text{m}}\text{Tc}$ (a ratio of 10^{-4}). The requirement for α -emitters is more stringent, 0.4 pCi/mCi of $^{99\text{m}}\text{Tc}$ (a ratio of 4×10^{-10}). Because of the difficulty in measuring this small amount of alpha activity in the eluate of a $^{99\text{m}}\text{Tc}$ generator, it may be more correct to say that there should be no detectable alpha contamination.

From the standpoint of product purity, the most attractive techniques for separating ^{99}Mo from irradiated targets appear to be adsorption chromatography using silver-coated carbon^{4-5,16-17} and Mo precipitation from mildly acidic solutions with α -benzoinoxime.^{4,18-19} In a more recent development, the use of an Ag-impregnated alumina column has been claimed to improve both the level of Mo recovery from U and the degree of product purity.²⁰

Purification of ^{99}Mo by α -Benzoinoxime Precipitation

The quantitative analysis of Mo by α -benzoinoxime precipitation (α -BP) of Mo(VI) is a standard gravimetric technique that has been used for over 50 years.^{19,21} Its use for recovery of ^{99}Mo from irradiated U targets was discussed in a 1974 patent.⁴ Experiments on α -BP have been run at ANL to measure the effect of increased U concentration and/or volume of the dissolver solution on recovery of ^{99}Mo and on separation from U, Np, Pu, and three fission products (I, Ag, and Cs).

Purification of ^{99}Mo from Uranium by α -BP

Molybdenum precipitation from solutions with varying amounts of uranium were performed using the procedure described by others.⁴ However, for these simulations, natural molybdenum and depleted uranium were used in place of ^{99}Mo and enriched uranium. In three of these experiments, following the second precipitation, the basic Mo-product solution was run through an ACAC column as a polishing step (also described by others).¹⁷ Conditions and results of these experiments are presented in Table 2.

Based on these results, there is no significant penalty for this precipitation procedure in yield of Mo product or decontamination from U due to higher U concentration or higher initial volumes of dissolver solutions. A single precipitation generally provides $\sim 10^{-5}$ decontamination in U and the Mo yield is $\sim 98\%$. A second precipitation continues to lower the U concentration; the overall Mo yield for two precipitation steps is $\sim 93\%$. Following the precipitations, running the redissolved Mo product through an ACAC column provided another order of magnitude of U decontamination.

Purification of ^{99}Mo from Np and Pu by α -BP

Based on the data in Table 1, the alpha-contamination level in the LEU produced ^{99}Mo product is equivalent to $1.2 \times 10^{-6} \text{ Ci } ^{239}\text{Pu/Ci } ^{99\text{m}}\text{Tc}$. This contamination is 3×10^3 higher than the $0.4 \text{ pCi}\alpha/\text{mCi } ^{99\text{m}}\text{Tc}$ specified for a fresh $^{99\text{m}}\text{Tc}$ generator and 4×10^4 higher than for an eluate sample from a 10-day-old $^{99\text{m}}\text{Tc}$ generator. Clearly, decontamination factors for neptunium and plutonium must be in the range of 10^4 to satisfy the $0.4 \text{ pCi}\alpha/\text{mCi } ^{99\text{m}}\text{Tc}$.

Table 2. Separation of Uranium from Molybdenum Using a Sequential Separation Scheme by (1) Precipitation, (2) Activated Charcoal, (3) Precipitation, and (4) Silver-Coated Activated Charcoal

Expt. No.	Initial Mass		First Precipitation ^a		Activated Charcoal Column		Second Precipitation ^b		Ag-Coated Activated Charcoal Column		
			Volume of Mo/U Solution, mL	Mass in Mo Product ^{c,d} mg	Mo	U	Mass in Mo Product, c, d mg	Mo	U	Mass in Mo Product, c, d mg	Mo
	Mo, mg	U, g									
1	2.23	7	100	2.24 (1.01)	0.41 (5.8x10 ⁻⁵)	ND ^f	ND	2.08 (0.93)	0.005 (7x10 ⁻⁷)	--	--
2	2.23	35	100	2.12 (0.96)	0.32 (9.2x10 ⁻⁶)	ND ND	ND ND	2.07 (0.93)	0.016 (5x10 ⁻⁷)	--	--
3	2.02	47	100	2.17 (1.07)	ND	1.97 (0.97)	2.9 (8.2x10 ⁻⁵)	ND	ND	2.10 (1.04)	3.2x10 ⁻³ (8.8x10 ⁻⁸)
4	2.02	47	500	1.47* (0.72)	0.55 (1.2x10 ⁻⁵)	1.41* (0.70)	0.55 (1.2x10 ⁻⁵)	ND	ND	1.48* (0.73)	2.1x10 ⁻³ (4.5x10 ⁻⁸)
5	2.02	47	500	ND	ND	ND	ND	ND	ND	1.80 (0.89)	1.7x10 ⁻³ (3.6x10 ⁻⁸)
6g	4.2	90	500	ND	ND	ND	ND	3.9 (0.93)	0.002 (2.10 ⁻⁸)	3.4 (0.81)	3x10 ⁻⁴ (3x10 ⁻⁹)

^a In all experiments, 15 mL of 2 wt % α -benzoinoxime in 0.4M NaOH was added for the precipitation step, except for Expt. 5, where 30 mL of chilled α -benzoinoxime solution was added.

^b 100 mL of acidic solution and 15 mL of α -benzoinoxime solution were used for all experiments. In Expts. 3-4, the α -benzoinoxime solution was chilled.

^c Values in parentheses are fractions of initial mass.

^d Mo analysis by ICP/AES; U analysis by a Scintex UA-3 Analyzer.

^e Low yield is due to a leak in the filter during first precipitation.

^f ND = not determined.

^g Dissolver solution also contained 8 mg of ²³⁹Pu and 4 mg of ²³⁷Np.

Experiments were run to measure separately the decontamination of Mo from Np and from Pu. In the Np experiment, 2.2 mg of Mo was separated from a 180-mL solution ($\text{H}_2\text{SO}_4/\text{HNO}_3$) containing 47 g U and 4.0 mg ^{237}Np using 20 mL of chilled 2 wt % α -benzoinoxime in 0.4N NaOH. After a single precipitation, the Np concentration was lower by a factor of 2.6×10^{-5} , which is essentially identical to the decrease found for UO_2^{2+} ion and sufficient to reduce Np to the specified level.

In a separate experiment, 4.2 mg of Mo was precipitated from a solution containing 90 g of U, 8 mg of ^{239}Pu , and 4 mg of ^{237}Np (see expt. 6, Table 2). In this experiment, the concentration of ^{239}Pu was lowered by:

- 1×10^3 by a single precipitation
- 6×10^3 by two precipitations
- 5×10^6 by two precipitations followed by an ACAC-column polishing step.

Although the precipitation technique does not appear to be as effective for decontamination from Pu as it is for that from U and Np (especially for the second precipitation), the use of the Ag-coated charcoal was quite effective as a polishing step. One precipitation followed by one ACAC-column polishing step should lower the plutonium level well below that needed.

Purification of ^{99}Mo from Fission Products by α -BP

The decontamination of Mo from three of the fission products that have been identified in ^{99}mTc generators (Ag^+ , Cs^+ , and I^-)* have been measured using the precipitation of Mo by α -benzoinoxime. For this study, tracer amounts of the radioisotopes ^{110}Ag , ^{137}Cs , and ^{131}I were added to carrier amounts of the same stable isotopes (90-100 $\mu\text{g}/\text{sample}$). The results of this study, presented in Table 3, show that the precipitation of Mo from HEU or LEU dissolver solution is equally as effective (or ineffective) for decontaminating the ^{99}Mo from these isotopes. Other separations are obviously used in current procedures to separate these elements from Mo. Because LEU and HEU ^{99}Mo solutions are nearly identical after precipitation, current methods are expected to be viable for LEU targets.

Table 3. Decontamination of Mo from Ag^+ , Cs^+ , and I^- by α -BP

Isotope	Decontamination Factor ^a	
	HEU	LEU
$^{110}\text{mAg}^b$	86 ± 7	101 ± 10
$^{131}\text{I}^c$	1.7 ± 0.1	1.8 ± 0.1
$^{137}\text{Cs}^d$	22×10^3	810 ± 220

^aError based on counting statistics only.

^bInitial activity = 1.88×10^8 dpm/mL.

^cInitial activity = 1.37×10^9 dpm/mL.

^dInitial activity = 2.29×10^8 dpm/mL.

*Radioisotopes of these three were readily available; experiments with other important fission products (e.g., Ru) are planned for the future.

Purification of ^{99}Mo by Ag-coated Activated Charcoal

Thus far our studies have been involved in finding the proper conditions for the U/Mo separation, and the separation is still not optimized for either Mo yield or purification from U. The data are therefore more preliminary and less reliable than for the precipitation method. However, trends are evident.

Purification of ^{99}Mo from Uranium by ACAC

Conditions and results of our best ACAC column separations experiments to date are presented in Table 4. These experiments were run using initial solutions described in Table 4 and a 1:1 ACAC/activated-charcoal column with a bed volume of $\sim 25\text{ cm}^3$, made up as described in the patent literature.¹⁷ After loading, the columns were washed with 100 mL of 0.41M H_2SO_4 , followed by ~ 10 mL of water. Molybdenum was stripped by 100 mL of warm 0.4M NaOH. Feed solutions for the second ACAC-column separations were prepared after removing 2.5 mL of the Mo-strip solution from the first column for Mo and U analysis by the addition of 3.6 mL of concentrated (18M) sulfuric acid.

Table 4. Mo Recovery and Purification from U Using ACAC

Experiment	<u>Initial Solution Composition^a</u>			<u>Strip Solution Composition</u>	
	Mo, mg	U, mg	Volume, mL	Mo, % Recovery	U, DF ^b
1	4.46	0	50	63.7	-
2	2.23	20,600	100	55.6	45
3	4.46	100,000	200	22.4	10
4	0	100,000	200	-	60 ^c
1' ^d	2.77	0	100	76	-
2'	1.21	252	100	77	120
3'	0.98	2350	100	56	160
4'	0	1650	100	-	260 ^c

^a Dissolved in 0.41M H_2SO_4 .

^b DF = decontamination factor = $(U_{\text{initial}}/Mo_{\text{initial}})/(U_{\text{strip}}/Mo_{\text{strip}})$.

^c Since Mo was not present, DF = $(U_{\text{initial}})/(U_{\text{strip}})$ only.

^d Strip solution from columns 1-4 were acidified and run through a second treatment; experiments are identified by the prime symbol.

Results of these experiments show that decontamination of Mo from U by ACAC-column separation is far less effective than by the precipitation method. Also, the higher the uranium concentration, the lower is the yield of molybdenum. Another disturbing feature of these separations was the high amounts of silver (86 mg in expt. 4) found in the Mo-product stream. This is clearly due to silver being stripped off of the column material with Mo. More work is necessary to refine ACAC preparation and to find proper conditions for this separation.

Purification of ^{99}Mo from Np and Pu by ACAC

We have yet to define conditions that produce the necessary high Mo yield and large decontamination factors from U. Data on the effectiveness of this method for purification of ^{99}Mo from Pu and Np await our finding these conditions.

Purification of ^{99}Mo from Fission Products by ACAC

Simulated solutions containing isotopes of Ag^+ , Cs^+ , and I^- were prepared similarly to those for the precipitation experiments. The solutions were passed through 2 x 4-cm columns of a 1:1 mixture of ACAC and activated charcoal and then washed with 100 mL of 0.8N H_2SO_4 and finally with about 5 mL of H_2O . The receivers were changed, and Mo was stripped from the columns with 100 mL of warm 0.4N NaOH . The stripped solutions were further purified by passing them through 1 x 5-cm ACAC polishing columns, followed by 20-mL rinses of 0.2N NaOH . The purified solutions were evaporated and diluted to 40.0 mL. A 20-mL aliquot of each solution was transferred to a plastic bottle for γ -counting.

The results of these experiments are presented in Table 5. Based on these results, higher uranium concentrations drastically reduce the effectiveness of the ACAC column for decontaminating Mo from silver and iodide ions. Decontamination from Cs^+ was high and essentially the same for both. Because the optimum conditions for Mo/U separation by ACAC columns are still to be realized, this work will need to be rechecked at a later date under these optimum conditions.

Table 5. Decontamination of Mo from Ag^+ , Cs^+ , and I^- by ACAC

Isotope	Decontamination Factor ^a	
	HEU	LEU
$^{110m}\text{Ag}^b$	$(2.7 \pm 0.2) \times 10^4$	$(2.9 \pm 0.1) \times 10^2$
$^{131}\text{I}^c$	$(4.5 \pm 0.1) \times 10^4$	$(6.5 \pm 0.1) \times 10^2$
$^{137}\text{Cs}^d$	$(1.5 \pm 0.1) \times 10^4$	$(1.1 \pm 0.1) \times 10^4$

^aErrors based on counting statistics only.

^bInitial activity = 1.88×10^8 dpm/mL.

^cInitial activity = 1.37×10^9 dpm/mL.

^dInitial activity = 2.29×10^8 dpm/mL.

Conclusions for Mo-Purification Studies

α -BP Purification

Decontamination of Mo from U, Np, and Pu, and three fission products (Cs, Ag, and I) by precipitation has been measured in a series of initial experiments testing the effectiveness of Mo precipitation by α -benzo-

inoxime. The results of these experiments lead us to conclude the following in processing LEU targets:

- There is no significant penalty in yield of ^{99}Mo .
- There is no significant penalty in the purification of ^{99}Mo from uranium.
- The use of an ACAC polishing step following precipitation of ^{99}Mo can further reduce contamination by uranium.
- Neptunium and plutonium can be removed to prescribed limits by a combination of precipitation and an ACAC polishing step.
- Separation of fission-product Ag^+ , Cs^+ , and I^- will be as effective (or ineffective) for LEU as for HEU targets.

ACAC Purification

Initial experiments on ACAC-column sorption/desorption separations have been made. Results from these studies show that chosen conditions were far from optimized. Molybdenum yields and separations from uranium were much lower than separation by Mo precipitation; however, ACAC-column separations from fission products are much better than by the precipitation method. A single separation step by precipitation followed by ACAC polishing step is likely to be the scheme of choice.

FABRICATION OF LEU TARGET

Several target designs with HEU are currently used for the production of fission product ^{99}Mo . These designs include curved plates^{1,2} and rods³ that contain either U-Al alloy or aluminide fuel and cylinders coated with a thin film of UO_2 on the inside surface.^{4,5} We anticipate that the curved plate and rod-type target designs will be able to utilize the high uranium densities achievable with the new LEU silicide fuels²² without changing the target geometries. However, the cylindrical target design currently uses a UO_2 surface density with HEU that is close to its practical fabrication limit. A new target design and/or a much denser film material is required for possible use of LEU. As a result, our efforts up to this time have concentrated on a cylindrical design with a layer of uranium metal electro-deposited on the inside surface.

Because it is not likely that required surface densities of UO_2 can be achieved with LEU, targets that are currently used for production of ^{99}Mo from electrodeposited UO_2 will not be satisfactory. In addressing potential solutions to this problem, we have considered several alternative approaches.²³ These approaches vary from utilization of a simple mechanical target support to the use of electrochemically plated uranium metal as the target material.

As a target material for ^{99}Mo production, a uranium metal target has several advantages over a UO_2 target. Its thermal conductivity is about an order of magnitude higher than UO_2 , its density is nearly a factor of 2 higher than UO_2 , and its plating efficiency from a molten salt bath is probably a factor of 5-7 higher than UO_2 from the aqueous system.

Disadvantages of using electrodeposited uranium metal targets are that they must be prepared from molten salt systems at high temperatures in inert atmospheres, and the deposit morphology tends to be dendritic. While the higher conductivity and density make uranium metal targets appear quite promising, one must remember the quantity of ^{235}U in the uranium metal target will be the same or higher, and heat management and safety problems are concerns that need to be thoroughly analyzed.

Electrodeposition of uranium metal from both fluoride²⁴⁻²⁸ and chloride²⁹⁻³⁵ salt melts have been discussed in the literature. The disadvantages of using molten fluoride salts are (1) the melts are extremely corrosive in nature, particularly at elevated temperatures; (2) the melt is extremely reactive to moisture; and (3) the high operating temperatures have a tendency to degrade the mechanical properties of the substrate material being plated. The fused chloride salts are less corrosive and can be used at lower temperatures. Therefore, electroplating uranium from chloride melts offers a promising approach from the point of view of material compatibility and low cost.

Recently, a new scheme for reprocessing metal reactor fuel has been proposed at ANL. A portion of this process utilizes a uranium and plutonium recovery step based on the electrochemical deposition of these metals from a molten salt.³⁴⁻³⁵ A molybdenum or iron cathode is used in conjunction with a solution of uranium in liquid cadmium that serves as the anode, and a molten electrolyte of LiCl-KCl-UCl_3 . The deposits formed are usually clusters of highly dendritic interwoven crystals. Several other electrorefining experiments were also conducted, using $\text{BaCl}_2\text{-CaCl}_2\text{-LiCl}$ (7.2-28.8-54.0 mol %) and $\text{BaCl}_2\text{-CaCl}_2\text{-LiCl-NaCl}$ (14.9-38.3-34.0-12.8 mol %). Both eutectic compositions contained small concentrations ($\sim 3\text{-}6$ wt %) of UCl_3 . Pure dendritic uranium deposits were obtained in practically every study.

The most promising chloride melts investigated appear to be the $\text{BaCl}_2\text{-KCl-NaCl}$ eutectic- UCl_3 and the $\text{BaCl}_2\text{-CaCl}_2$, LiCl-NaCl eutectic- UCl_3 systems. Additions of small quantities of alkali metal fluorides may be helpful in improving the quality of the metal deposit. Serious problems that need to be addressed are the dendritic morphology of the uranium deposit and the adhesion of that deposit to the metal substrate. Several variables need to be optimized if a dense electrodeposit of pure uranium is to be produced. These variables include substrate material, substrate preparation, current density, electrolyte composition, plating temperature, and width and frequency of nucleating pulses.

DEMONSTRATION OF URANIUM METAL DEPOSITION ONTO STAINLESS STEEL

Experimental

Electroplating of the uranium metal was performed in a helium-atmosphere glove box. A detailed procedure for this operation can be found elsewhere.²³ The cathode was a rectangular Type 304 stainless steel coupon (height x width, 2.9 cm²; thickness, 0.64 mm) that was polished through 0.3 μm Al_2O_3 powder. The anode was a rectangular uranium foil (height x width, ~ 3.75 cm²; thickness, 0.88 mm). The molten salt electrolyte was the quaternary system, $\text{BaCl}_2\text{-CaCl}_2\text{-LiCl-NaCl}$ (36.60-41.92-14.18-7.30 wt %) with approximately 6 wt % UCl_3 , which was generated in situ by the oxidation of metallic uranium pins with CdCl_2 . The CdCl_2 and quaternary eutectic salt

were polarographic-grade materials obtained from Anderson Physics Laboratories, Urbana, IL. The metallic uranium was depleted material. The cell temperature was controlled to within 0.5°C.

Before deposition began, the cell crucible was loaded with 450 g of the quaternary salt and 24 g of CdCl_2 and heated to 475°C. Depleted uranium (28 g) was added to the molten salt and heated overnight with stirring to generate the UCl_3 and cadmium metal from the CdCl_2 and uranium metal. The stirrer was then removed from the cell, and the electrodes were installed for the uranium metal target preparation.

Four electrodeposition tests were conducted. In each study, the total charge passed was ~ 750 mA-h or ~ 259 mA-h/cm² of cathode front surface. Three of the experiments were performed at constant current densities (22.4 mA/cm² for 12.17 hours, 53.5 mA/cm² for 4.83 hours, and 105 mA/cm² for 2.5 hours), and one experiment used pulse plating. In the pulse-plating experiment, the cathode was anodized at 120 mA, followed by a 15-s rest period. Four cycles of nucleation pulsing were then applied, each cycle consisting of 15 s of current application peaking at 360 mA, followed by a 15-s rest period. For the remainder of the deposition period, high-frequency DC pulsing was applied; each cycle consisting of 100 ms of current application peaking at 175 mA, followed by a 40-ms rest period. Total time was 6 h, and the time-averaged current density was ~ 43 mA/cm². If one assumes that 70% of uranium is plated on the front surface and the coulombic efficiency is 70% (both reasonable assumptions), then the deposit, assuming theoretical density, would be 2.0×10^{-2} cm thick and contain ~ 74 mg of ^{235}U /cm², which would correspond to ~ 30 g of ^{235}U for a 400-cm² target.

Results & Conclusions

Uranium was deposited on the cathode in all of the tests. Although most of the deposited uranium was found on the side of the cathode that was facing the anode, a significant amount was also found on the back side. The effect of current density on the morphology of the deposits on the stainless steel surface showed a clear trend. At the lower current densities, the deposits were denser and more evenly distributed on the electrode surface, and the dendrites were smaller. Prior anodization of the stainless steel appeared to have little effect on the morphology or adhesion of the deposit. The deposit obtained with the pulsed current was similar to that obtained at the lower current density, but tended to be slightly more bonded to the substrate. The pulse-plated uranium deposit is shown in Fig.1.

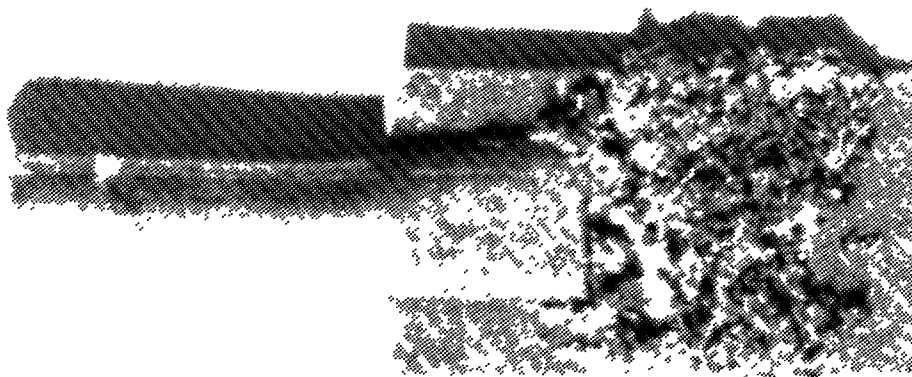


Fig. 1. Electrodeposition of Uranium by Pulsed Plating

The uranium deposits were found to dissolve readily in a sulfuric acid- H_2O_2 solution with vigorous gas evolution. These results indicate that the uranium metal deposits dissolve readily in the acid dissolution media being used in the current process for UO_2 targets.⁴⁻⁵

The dendritic nature of the uranium deposits and bonding of the deposits need to be improved. To address these problems, the effect of the following variables on morphology and adhesion need to be investigated: (1) substrate material and temperatures on crystal morphology and adhesion; (2) surface preparation on morphology; (3) electrolyte composition and its U(III) content on crystal morphology; (4) electrolyte flow and/or target substrate rotation on crystal morphology and adhesion; and (5) current density, direct and pulsed. The optimization of each of the variables described above could lead to a viable process for LEU target preparation.

EFFECTS OF LEU TARGETS ON RADIOACTIVE WASTE GENERATION

Three potential effects on radioactive waste generation exist if LEU rather than HEU is used for the production of ^{99}Mo :

1. Increased amounts of irradiated-uranium by-product that must be solidified, stored, and transported to a reprocessing plant.
2. Increased radioactive waste generation (spent chemicals and equipment, wipes, labware, etc.) due to processing more uranium for the same ^{99}Mo yield.
3. Increased amounts of ^{239}Pu and other transuranic elements, causing waste to be designated as TRU (i.e., not as low-level) waste, thus increasing the cost and difficulties of disposal.

These issues can be analyzed by comparing the reference HEU and LEU targets described in Table 1. The data in Table 1 indicate that, to produce the same amount of ^{99}Mo , almost six times the amount of uranium must be dissolved, thus increasing the dissolver solution by a factor of three to six. The processing scheme for separating and purifying ^{99}Mo from actinides and other fission products is a multistep procedure. In the acidic dissolution process, the first separation/purification step removes the ^{99}Mo product from the irradiated-uranium by-product and many other contaminants. Further processing steps of the ^{99}Mo product are necessary to purify ^{99}Mo from other fission-product and transuranic contamination.

Irradiated-Uranium By-Product

The irradiated-uranium (LEU or HEU) by-product solution from the first separation/purification step would likely be heated to dryness, stored, and/or be sent to a reprocessing plant. Assuming this solid would be in the form of $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and/or $\text{UO}_2\text{SO}_4 \cdot 3\text{H}_2\text{O}$, the mass of the U waste from a HEU target would be ~30 g with a specific activity of 2×10^3 nCi α/g and from a LEU target would be 180 g with a specific activity of 4.4×10^3 nCi α/g . The β/γ activity would be nearly identical for both, with the β/γ specific activity of the spent LEU being ~1/6 that of the HEU. The specific activity differences are inconsequential, but the processing of LEU does necessitate storage and transportation of six times the volume of uranium/fission product salts.

Increased Waste Generation

If, during the first separation/purification step, precipitation of α -benzoinoxime is used to separate ^{99}Mo from the solution, a larger filter may be required. If a column separation is used, a larger column bed may be required to adsorb the Mo. After the first separation step, except for the possible need to purify from the higher concentrations of plutonium, no difference will exist between the HEU- and LEU-produced ^{99}Mo product stream. The uranium content of the ^{99}Mo product of the first separation will be about the same, as will the contamination by other fission products. Therefore, the waste generated in the many follow-up purification steps would be similar for LEU and HEU targets. An increase in waste volume caused by processing LEU targets through all processing steps should be in the range of 0-30%, rather than a factor of six based solely on increased U in the target.

Increased TRU Content

The United States Nuclear Regulatory Commission (NRC) in 10 CFR Part 61³⁶ and Environmental Protection Agency (EPA) in 40 CFR Part 191³⁷ have specified the limit to the transuranic element (TRU) specific activity of low-level waste (LLW) to be 100 nCi α /g waste; other such regulations dealing with TRU content are likely in place throughout the world. Because there will be ~26 times more ^{239}Pu produced in LEU targets than in HEU targets with comparable ^{99}Mo yield, there is a concern that waste currently disposed of as LLW may be reclassified as TRU waste, thus causing more difficulty in its disposal and increasing waste disposal costs.

We estimate that the processing of LEU targets will result in a twenty-six fold increase in ^{239}Pu and a possible increase of 0-30% in waste volume. Thus, for the LEU-generated waste to be nonTRU (i.e., LLW), the current HEU-generated waste must contain ≤ 4 nCi ^{239}Pu /g. Because it is extremely difficult to measure specific activities ≤ 10 nCi/g and because sophisticated techniques and equipment are required to discriminate between α -particles from ^{239}Pu and ^{235}U (which produces 55% of the α activity in spent HEU and is not considered as TRU), current industry TRU-contamination values are almost certainly estimates and not measured quantities. Assuming that most estimates of contamination are conservative, LEU radioactive waste may remain LLW.

Conclusions

Processing LEU targets would produce approximately six times the amount of irradiated uranium by-product for the same yield of ^{99}Mo from a HEU target and may generate more LLW, but the increase is estimated to be in the range of 0-30% rather than a factor of 6. Also, the increased ^{239}Pu content in irradiated LEU targets may not make the waste a TRU-containing waste and, therefore, may still be eligible for LLW disposal.

SUMMARY

Although the reported results are preliminary, there is reason to be optimistic about the feasibility of utilizing LEU targets for the production of ^{99}Mo .

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CONTINUING INVESTIGATIONS FOR TECHNOLOGY ASSESSMENT OF ^{99}Mo PRODUCTION FROM LEU TARGETS*

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Abstract

Currently much of the world's supply of $^{99\text{m}}\text{Tc}$ for medical purposes is produced from ^{99}Mo derived from the fissioning of high enriched uranium (HEU). This paper presents the results of our continuing studies on the effects of substituting low enriched uranium (LEU) for HEU in targets for the production of fission product ^{99}Mo . Improvements in the electrodeposition of thin films of uranium metal continue to increase the appeal for the substitution of LEU metal for HEU oxide films in cylindrical targets. The process is effective for targets fabricated from stainless steel or zircaloy. Included is a cost estimate for setting up the necessary equipment to electrodeposit uranium metal on cylindrical targets. Further investigations on the effect of LEU substitution on processing of these targets are also reported. Substitution of uranium silicides for the uranium-aluminum alloy or uranium aluminide dispersed fuel used in current target designs will allow the substitution of LEU for HEU in these targets with equivalent ^{99}Mo -yield per target and no change in target geometries. However, this substitution will require modifications in current processing steps due to (1) the insolubility of uranium silicides in alkaline solutions and (2) the presence of significant quantities of silicate in solution. Results to date suggest that substitution of LEU for HEU can be achieved.

INTRODUCTION

Technetium-99m for medical purposes is a decay product of ^{99}Mo , which is produced in research reactors from the fissioning of ^{235}U or from neutron capture in ^{98}Mo . This continuing effort is related only to fission-product ^{99}Mo .¹ Presently, ^{99}Mo is produced using a variety of target designs that contain HEU ($\sim 93\% \text{ }^{235}\text{U}$). These designs include curved fuel plates,^{2,3} rods,⁴ and cylinders with a film of UO_2 electroplated on the inside surface.^{5,6}

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The purpose of this study is to assess the feasibility of substituting LEU for HEU in targets for production of fission-product ^{99}Mo . The main areas addressed this year were (1) optimization of conditions for electrodeposition of uranium metal to produce well-bonded, uniform, dendrite-free, 0.3 mm films that are compatible with current target designs using UO_2 films, (2) the effects of LEU substitution on the processing of ^{99}Mo from these targets, and (3) the dissolution (by bases) of uranium silicide targets followed by separation and purification of ^{99}Mo . This paper reports on the present status of our investigations.

FABRICATION OF LEU METAL TARGET

Several target designs with HEU are currently used for the production of fission product ^{99}Mo . These designs include curved plates^{2,3} and rods⁴ that contain either U-Al alloy or aluminide fuel and cylinders coated with a thin film of UO_2 on the inside surface.^{5,6} We anticipate that the plate and rod target designs can be converted to LEU by utilizing the high uranium densities achievable with the new LEU silicide fuels⁷ without changing the target geometries. However, the cylindrical target design with HEU currently uses a UO_2 surface density that in some cases is close to the target's practical fabrication limit. A new target design and/or a much denser film material is required for use of LEU. As a result, our efforts have concentrated on a cylindrical design with a thin layer of uranium metal electrodeposited on the inside surface.

Uranium metal targets for fission ^{99}Mo production have several advantages over the UO_2 targets. For example, uranium metal is about twice as dense as UO_2 , its thermal conductivity is an order of magnitude higher than UO_2 , and its plating efficiency from LiCl-KCl-UCl_3 molten salt melts is 100% vs. 20% for the UO_2 deposition process. The principal disadvantages of using electrodeposited uranium metal targets are that (1) they must be prepared from molten salt systems at high temperatures ($\sim 450^\circ\text{C}$) in an inert atmosphere, and (2) the deposit morphology tends to be dendritic. While the higher conductivity and density make uranium metal targets appear quite promising, heat management and safety issues need to be thoroughly analyzed.

Published literature indicates that uranium metal can be electrodeposited from either a fluoride⁹⁻¹³ or chloride^{8,14-18} molten salt. Because the fluoride melts are more corrosive, more sensitive to moisture, and operate at much higher temperatures than the chloride melts, electroplating uranium metal from chloride melts offers advantages over the fluoride melts. While many different base chloride salts containing UCl_3 have been used to plate uranium metal ($\text{BaCl}_2\text{-CaCl}_2\text{-LiCl}$, $\text{BaCl}_2\text{-KCl-NaCl}$, $\text{BaCl}_2\text{-CaCl}_2$, LiCl-NaCl , and LiCl-KCl), none seems to offer a significant advantage over any other. Because the LiCl-KCl eutectic is inexpensive and readily available commercially, it was chosen as the base electrolyte for our studies.

This investigation evaluated the effects of current density, plating mode (direct current vs. pulse current), and metal substrate material on the quality of the uranium deposit. Initial studies evaluated the quality of the uranium deposits that were formed under direct current plating conditions using a nickel substrate material.

Pulse-plating regimes were next investigated in an effort to optimize the plating regime. In these latter studies, factorial investigations were conducted to identify a regime where dendrite-free deposits are formed. Once these studies were completed, pulse-plating electrodeposition of uranium films was carried out on a variety of substrate materials. Preliminary studies with stainless steel, carbon steel, and zircaloy indicated these materials gave poorly bonded, poor quality uranium deposits. Therefore, the emphasis of the research shifted to nickel and copper substrate materials because they are fairly resistant to air oxidation and make excellent precoating materials for either stainless steel or zircaloy cylinders. Both materials may be electrochemically deposited on stainless steel^{19,20} or zircaloy or, in the case of nickel, by electroless plating methods.²¹ Intermetallic compound formation²² between nickel or copper and uranium is expected to result in good adhesion of the deposit to the substrate.

Electrochemical parameters investigated in our pulse-plating studies included the effect of a nucleation pulse and surface anodization prior to uranium pulse deposition. Nucleation pulses were proposed earlier by other investigators as a tool to enhance coating uniformity,²³ while surface preanodization has been proposed as a means to generate a clean surface for deposition.²⁴ A cost estimate for equipment to run a full-scale electrodeposition process is provided at the end of this section.

Experimental

Uranium metal was electrodeposited from molten salt in a helium atmosphere glove box. The cathode substrates used in constant-current and later pulse-plating experiments were disk-shaped coupons of metal (zircaloy, stainless steel, carbon steel, nickel, or copper) that were 1.6 cm in diameter and 1 cm high (total exposed surface area = 6.2 cm²). Early pulse-current experiments were run with smaller (0.5 cm diameter) disks because of equipment limitations. The cathode was rotated at ~300 rpm for constant-current experiments and was kept stationary for pulse-plating experiments.

The bottom circular face of the coupon was polished for five minutes with, in succession, 600-grit SiC paper, 6 μ m diamond paste, 0.3 μ m alumina slurry, and 0.05 μ m alumina slurry. The resulting surface was degreased with acetone and rinsed with distilled water. The coupons were then etched for 30 sec with a reagent of 4 vol % concentrated HNO₃ and 10 vol % CH₃COOH diluted by H₂O.

The reference and counter electrodes used in these experiments consisted of 15 cm lengths of 0.8 cm diameter uranium rods. The molten salt electrolyte was LiCl-KCl eutectic (44.2-55.8 wt %) with approximately 20 wt % UCl₃, which was generated in situ by the oxidation of metallic uranium pins with CdCl₂. The CdCl₂ was reagent grade material from Cerac, Inc., Menomonee Falls, WI, and the anhydrous LiCl-KCl eutectic was from Lithcoa, Bessemer City, NC. Plating studies were conducted at 435°C.

Experimental Results

Direct Current Plating Studies

The experimental conditions for these plating studies, which included current densities of 5, 10, and 20 mA/cm² and plating times of 2.75 to 13.0 hours, produced uranium films between 100 and 330 mg/cm². During the course of these studies, the coulombic efficiency of the plating process was found to be essentially 100 percent, and the quantities of uranium deposited were determined based on this observation. The results indicate that at higher current densities (20 mA/cm²) there was a greater tendency to form dendrites, which were 2-3 mm in length. At lower current densities (5 mA/cm²) and long plating times, the electrodeposit was less dense, with significant areas free of deposit. From these studies, it would appear that, under constant-current plating conditions, a 10 mA/cm² current density is near optimal. The uranium deposits formed at 10 mA/cm² had excellent bonding and may be adequate for fabrication of uranium targets for ⁹⁹Mo production.

Pulse-Plating Studies

A series of experiments was performed using the smaller Ni cathode to find the pulse-plating conditions that provide the highest possible deposition rate for a dendrite-free uranium deposit. The condition was found to be cycling between a pulse at -65 mV for 0.1 msec followed by a zero potential pulse for 1 msec. Using this regime, twenty-one hours is required to deposit a 0.3 mm (580 mg U/cm²) film of uranium. Thinner films require proportionally shorter times.

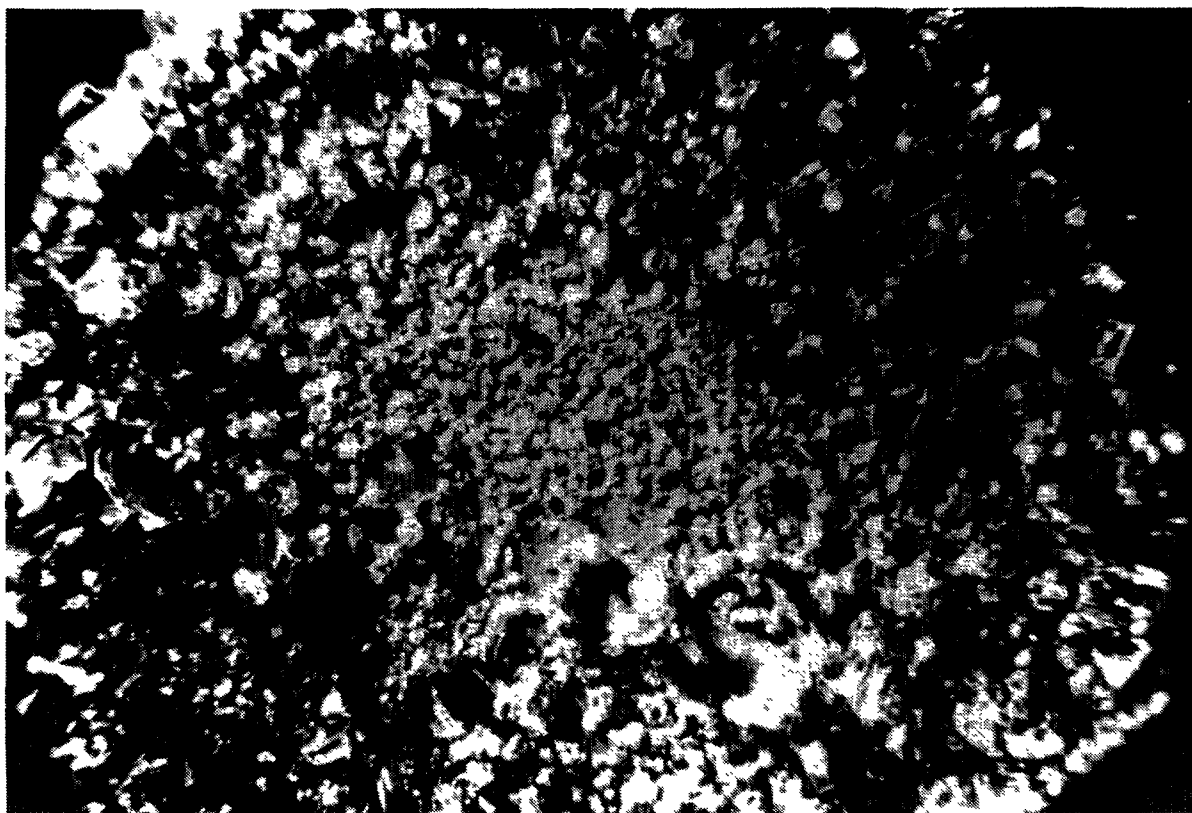


Fig. 1. The Best Uranium Deposit on Nickel Coupon To Date.

Under these conditions, a second series of experiments was performed to measure (1) the success of this method on electrodepositing uranium metal films on various substrates (stainless steel, carbon steel, zircaloy, nickel, and copper), and (2) benefits in uniformity gained by preanodization of the substrate and by use of a nucleating pulse. Nickel and copper substrates were clearly superior to the other metal coupons tested in bonding and uniformity. Overall, a nickel substrate was the better of the two.

The use of preanodization of the nickel and a nucleation pulse improves the uniformity of the deposit. The best deposit laid down to date is shown in Fig. 1. The deposit is nominally 0.3 mm thick, with a variation in thickness between 0 and 0.4 mm. This sample was prepared by use of a preanodization step of 5 coulombs at 1.35 V, followed by a -706 mA/cm^2 nucleation pulse for 2 sec, followed by 21-hour deposition. After deposition of uranium on the coupon in the helium atmosphere box, the solidified electrolyte was removed from the coupon by washing in the open atmosphere with 0.01N HCl, distilled water, absolute ethanol, and acetone. The uranium appeared metallic with no signs of oxidation after two hours in the laboratory atmosphere. The bonding of the deposit to the substrate was excellent.

Further studies are needed to reduce plating times and to improve the uniformity of the uranium deposit. In the latter case, studies are needed to optimize the nucleation pulse and preanodization regimes.

Work is also needed to design and test the plating cell for the fabrication of the cylindrical targets. Studies are also needed to examine nickel preplating of the stainless steel and zircaloy target cylinders. This nickel plating may well be done commercially by an electroless plating process.

Cost Analysis for Uranium Metal Target Fabrication

A cost estimate for the equipment and chemicals needed for an operational system completely set up for uranium-metal deposition on a cylindrical target is shown in Table 1. This system could electrodeposit uranium metal films on 2-6 cylinders simultaneously. Under our presently optimized plating regime, the system would produce 2-6 cylinders per day. Quotations on the major items (glovebox system, purification system, and furnace units) were received from Vacuum Atmospheres Company, Hawthorne, CA, and from Lindberg, Watertown, WI. Quotations on the cost of nickel electroless preplating of the inner walls of target cylinders were received from TWR, Rosemont, IL. Cost estimates on the electrochemical plating equipment and the other smaller items, such as the plating cell and chemical cost, were derived from standard electrical units and/or auxiliary equipment and chemicals and materials used here at the Argonne National Laboratory. The cost estimate from TWR on a 1 mil-thick nickel electroless preplating of stainless steel or zircaloy target cylinders was \$14 each.

In summary, it will cost approximately \$125,000 to place into operation a uranium metal plating system for cylindrical targets for the production of ^{99}Mo . It should be noted that the nitrogen and moisture analyzers included in this cost estimate are convenient but are not essential.

Table 1. Equipment Cost for Target Fabrication

Item Description	Total Price, \$
DXL-002-S-P Dri Lab Glovebox Stainless Steel, 90-in. wide x 30-in. deep x 33-in. high, with auxiliary equipment	14,750
Mo-40-2V Dri-Train Dual Bed Purifier and Auxiliary Equipment for oxygen and moisture removal	16,815
Ni-40 Ni-Train and Auxiliary Equipment for nitrogen and/or hydrogen removal	19,460
Instrument	
A-1 Nitrogen Analyzer	
AM-2031 Moisture Analyzer	
AO-316-C Oxygen Analyzer	
AA-Audio Alarm	
ANL-1R Chart Recorder	
AV-1 Automatic Antechamber Control	
OP-30 Quick Purge	24,450
Electrical connections, wiring, breakers, etc.	3,850
Two Reactor Furnace Tubes with connecting flange (6-in. O.D. x 30-in. length)	1,000
Fabrication and installation of two flanges in glovebox floor for furnace tubes	1,000
Factory Engineer for start-up, demonstration and training of operators	2,850
Two Lindberg Model 54-M6024-Z	
Three Zone Hinged Furnace with controller and auxiliary equipment	16,554
Electrochemical plating equipment	10,000
Cell housing, chemicals, ceramic beakers, etc.	<u>15,000</u>
<u>TOTAL</u> Cost of Target Fabrication System Facility	\$125,729

PROCESSING OF LEU METAL TARGETS

Patented processes for separating and purifying ^{99}Mo from cylindrical UO_2 film targets describe methods for dissolving the irradiated uranium material in acid and separating ^{99}Mo from uranium, transuranic elements, and other fission products.^{1,5,6,25} The first separation/purification step for this process involves the use of either (1) precipitation of Mo by α -benzoinoxime or (2) adsorption of Mo by Ag-coated

activated charcoal (ACAC) columns. Because the greater amount of uranium in LEU vs. HEU targets is especially important in this initial separation step, much of the work reported in Ref. 1 was directed to these two techniques. The results¹ showed that the precipitation process would not be hampered by the use of LEU, but the ACAC column separation was likely to be. This earlier work left two further concerns to be addressed. The first was the effect of higher amounts of uranium on the behavior of fission product ruthenium in these two separation techniques. The second was optimizing the less-than-satisfactory performance of the ACAC column separation for processing HEU or LEU targets. The following sections discuss our efforts in resolving these two concerns.

Separation of ⁹⁹Mo from Ruthenium

Experimental

The separation of ⁹⁹Mo from ruthenium was measured for both α -benzoinoxime precipitation and ACAC column adsorption under conditions similar to those presented in Ref. 1 for processing of LEU and HEU targets. Acidic solutions of natural molybdenum and depleted uranium were spiked with ¹⁰³Ru for these studies. Ruthenium-103 was measured by gamma counting using a GeLi detector.

Results

α -Benzoinoxime--The fraction of ¹⁰³Ru activity that remained with Mo after the precipitation of 0.5 mg Mo from 50 mL of solution by α -benzoinoxime was: 0.4% for 11.9 g U, 1.3% for 7.1 g U, and 3.5% for zero U. The trend in greater purification of Mo from Ru with greater amount of uranium indicates that use of LEU may reduce the chances for Ru contamination in the ^{99m}Tc product.

ACAC Columns--Four experiments were performed to test the effectiveness of ACAC column sorption of Mo for its separation from Ru. The results of this study, presented in Table 2, show that it is not as effective as

Table 2. Separation of Ru from Mo using ACAC Adsorption of Mo

Initial Conditions ^a		% Ru			Ratio % Ru Recovery ^c % Mo Recovery
		In Mo Product	In Eluted Feed	Remaining ^b on Column	
[U], g	[H ⁺], N				
0	0.6	10.9	53.9	35.2	0.13
7.12	0.6	7.2	45.3	47.5	0.13
7.12	0.4	5.6	42.0	52.4	0.075
11.90	0.4	10.9	38.0	51.1	0.19

^a In 50 mL, 0.503 mg Mo in each experiment.

^b Calculated from initial feed minus the sum of that in the eluted feed and the Mo product solution.

^c In Mo product stream.

the precipitation technique. Further, it appears that part of the Ru passes through the column during the Mo adsorption step, part is eluted with the Mo product, and part remains bound to the alumina after Mo is desorbed. There is no clear trend in the data, except that Ru is not very well separated from Mo by ACAC columns.

Optimization of ACAC Columns

Further studies were performed to attempt optimization of ACAC column recovery of Mo. Fresh column materials were prepared and separations were performed using instructions and suggestions in the literature.^{5,6,25,26} As reported in Ref. 1, separations from uranium are not as good or as consistent as those attainable by the precipitation method, especially with uranium concentrations equivalent to those encountered by a first Mo separation step for processing of either LEU or HEU targets. Stripping of silver from the column material was noted for feeds containing high uranium concentrations. This stripping occurred with evolution of gas bubbles, which tend to destroy column effectiveness. As reported earlier, ACAC column separations are useful as a polishing step, after most of the uranium is removed by α -benzoinoxime precipitation of Mo. However, we conclude that these columns are not likely to be used commercially as a primary U/Mo separation, and we are planning no further work on them.

PROCESSING OF LEU SILICIDE TARGETS

It appears possible to convert current HEU targets that use aluminum alloy or uranium aluminide to LEU by use of uranium silicides without changing target geometries or sacrificing ⁹⁹Mo irradiation yields. The following is a summary of our studies into modifications in current technology that may be necessary to process irradiated LEU silicide targets using basic dissolution. The current processing of HEU targets^{27,28} is likely to include dissolving the cladding and meat of the irradiated target in 2-5M NaOH. In this step uranium and many of the fission products precipitate as hydroxides; ¹³³Xe is released and collected; and other species, including Mo, are solubilized in the aqueous solution. As the pH is decreased by the addition of acid, ¹³¹I is released from solution as a gas. The acidified solution is then run through an alumina column, where Mo is sorbed. Molybdenum is subsequently eluted from the column and further purified.

Concerns in processing of LEU silicide targets arise from (1) the greater amount and different composition of uranium to be processed, (2) the presence of alloying elements that are necessary in the cladding of silicide fuel plates, and (3) the presence of significant quantities of silica in process solutions. The effects of these concerns on each processing step are discussed below.

Target Dissolution

Dissolution studies were performed using unirradiated miniplates and miniplate components (Al6061 cladding material, aluminum powder, and depleted uranium U₃Si and U₃Si₂). The miniplates and their components were supplied by R. F. Domagala and coworkers, Argonne National Laboratory.

Solid mixtures of Al6061 cladding, aluminum powder, and either U_3Si or U_3Si_2 were heated with 3M NaOH solution. Dissolution of the cladding and aluminum powder was rapid but controlled; the uranium silicides appeared not to dissolve at all. They also were insoluble in 6M NaOH and 3M NaOH/4M $NaNO_3$ solutions. The formation of copious amounts of black precipitate resulted from the precipitation of hydroxides of some of the alloying elements in Al6061 cladding (nominal composition is reported in Table 3, all other elements are 0.05 wt % max with their total being 0.15 wt % max; the balance is Al). The composition of the cladding calculated from the sum of the compositions of the alkaline precipitate and supernatant (Table 3) agrees with the specified composition of Al6061. The major metallic constituent of the precipitate was aluminum (83 to 92 wt %); other metals contained in the precipitate are also reported in Table 3. Probably because of some complexation by hydroxide ion, the precipitation of alloying-element hydroxides was not complete; the extent of their precipitation is reported in the second column of Table 3.

Table 3. Fate of Alloying Elements in Al6061 Cladding during Alkaline Dissolution of Uranium Silicide Targets

Weight % of Composition				
Element	% of Element Precipitated	Alkaline Precipitate ^a	Alkaline Precip. plus Supernatant ^b	Al6061 Cladding ^c
Al	28	83-92	96	95.9-98.6
Mg	99	4.6-8.0	1.1	0.8-1.2
Si	18	2.9-4.5	1.8 ^d	0.4-0.8
Fe	94	1.5-1.9	0.5	0.7 max
Cr	48	0.6-1.1	0.2	0.04-0.35
Cu	94	0.4-0.7	0.2	0.15-0.40
Mn	97	0.3-0.4	0.1	0.15 max
Zn	67	0.2-0.3	0.1	0.25 max
Ti	78	0.1	0.04	0.15 max

^a Range from two experiments, performed under slightly different conditions.

^b Experiments dissolved both the requisite amount of Al6061 cladding and Al powder for uranium-silicide dispersed fuel.

^c Based on manufacturing specifications, from R. Domagala, ANL.

^d This higher than expected value (from the Al6061 composition) is likely due to some dissolution of glassware.

More drastic measures than heating with concentrated base alone are necessary to dissolve the U_3Si and U_3Si_2 materials. A 1/1 solution of 3M NaOH/30% H_2O_2 readily dissolved these materials with heating. Hydrogen peroxide not only dissolves uranium, it also complexes it and prevents it from precipitating. After dissolution of the uranium silicides is complete, H_2O_2 must be destroyed to allow precipitation of uranium (thus separating it from the soluble molybdenum) and to prevent complications in downstream processing of the Mo. Destruction of the peroxide can be accomplished by the addition of hydroxylammonium chloride (HAC), but its addition must be carefully controlled. If too much HAC is added, it too will complex uranium and prevent its precipitation. Addition of small quantities of acidic ferric nitrate solution (10^{-2} mol Fe/mol U) was found to catalyze the auto-degradation of peroxide but did not take the reaction to completion. The addition of potassium permanganate will complete the destruction of H_2O_2 and allow complete precipitation of uranium hydroxide. Lowering the pH to ~8 will allow the precipitation of MnO_2 .

If ^{99}Mo were not leached from the irradiated uranium silicide fuel particles during basic dissolution of the cladding and the aluminum matrix, it would be possible to have a two-step process. Because of their much lower density, the precipitated alloying-element hydroxides can be easily swirled away, leaving the high density uranium silicides behind for further processing. After the separation is complete, the silicides can be dissolved independently with alkaline peroxide. We plan to test this process using low-burnup targets in 1988.

Acidification

Before molybdenum can be separated from the dissolver solution, the pH of the dissolver solution must be decreased with the addition of acid. Acidification to a pH of ~3 causes the precipitation of aluminum; this precipitate redissolves as more acid is added. To prevent the precipitation of gelatinous silica, the concentration of silicate in solution must be kept at or below ~0.1M.

Adsorption of Mo on Alumina

Molybdenum can be separated from other components of the acidified dissolver solution by its adsorption on a bed of alumina. Molybdenum can then be stripped from the column by a concentrated alkaline solution. Experiments were run to measure the effect of the concentrations of hydrogen ion, uranium, and silica on Mo adsorption by alumina. Representative data on their effects on the distribution ratio (K_d) between alumina and aqueous solutions are presented in Figs. 2, 3, and 4, respectively. The higher the distribution ratio, the better Mo is sorbed to the alumina, and the smaller the alumina column must be. The sorption of Mo on alumina is highly dependent on the concentration of Mo in solution. Molybdenum(VI) has an extremely complex solution chemistry due to polymer formation.^{29,30} It appears that the MoO_4^{2-} monomer and smaller polymers sorb better than larger polymers. Therefore, Mo sorption is highest at lower Mo concentrations.

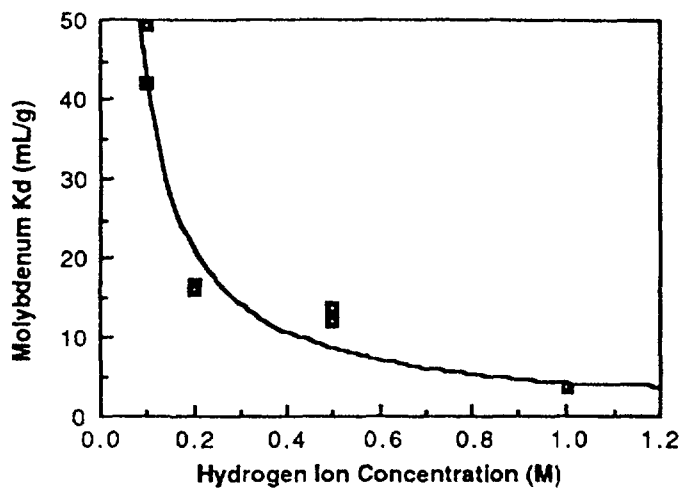


Fig. 2. Effect of Hydrogen Ion Concentration on Mo Adsorption.
[Mo] = $7 \times 10^{-4} \text{M}$.

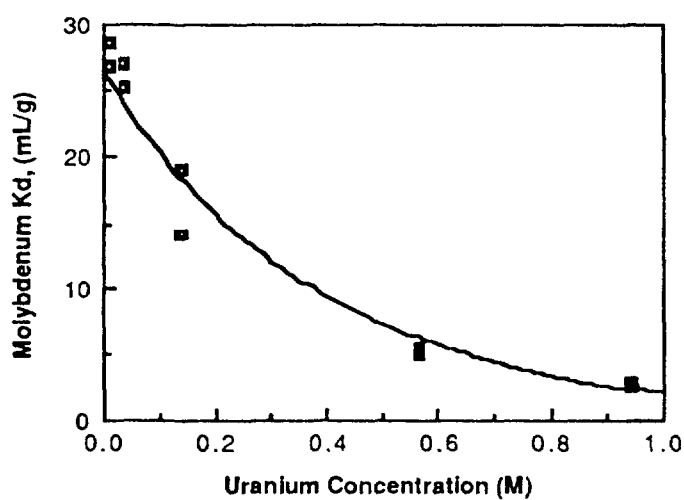


Fig. 3. Effect of Uranium Concentration on Mo Adsorption.
[Mo] = $1.4 \times 10^{-3} \text{M}$,
[H⁺] = 0.5M .

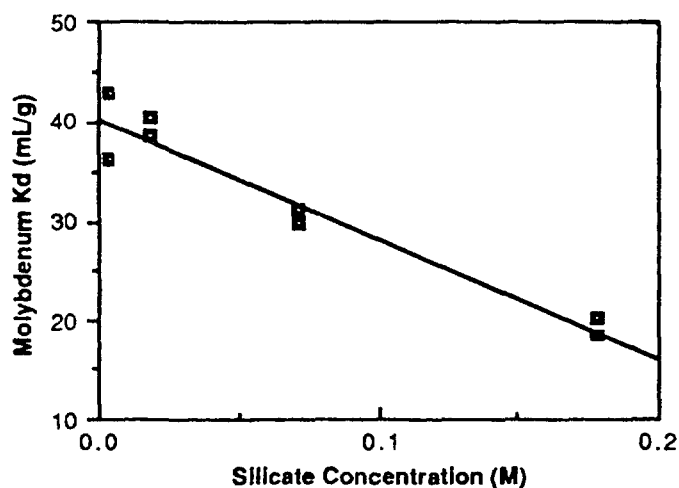


Fig. 4. Effect of Silicate Concentration on Mo Adsorption.
[Mo] = $2.0 \times 10^{-3} \text{M}$,
[H⁺] = 0.5M .

Under conditions envisioned for processing LEU-silicide targets (essentially complete precipitation of uranium and $[Si] \leq 0.1M$), the concentrations of these species will allow satisfactory sorption of Mo on alumina columns.

CONCLUSIONS

LEU-Metal Targets

Improvements have been made in the electrodeposition of uranium metal films for application with LEU targets. Well-bonded, dendrite-free uranium films can be electroplated onto stainless steel or zircaloy targets by use of a thin (0.02 mm) preplate of nickel on these metals. Increases in uranium-film uniformity by preanodization of the nickel substrate and by pulse nucleation of uranium have been achieved but have not yet been optimized. We believe that uranium films that we have electroplated on a laboratory scale will be suitable for commercial LEU target fabrication. In 1988, we plan to fabricate down-sized cylindrical targets using this technique.

The separation of fission-product ruthenium from ^{99}Mo by the α -benzoioxime precipitation of Mo appears to be enhanced by the use of LEU. Our continuing studies on processing of LEU targets for ^{99}Mo production have reinforced our belief that there will be no significant barriers in target processing due to the substitution of LEU for HEU.

LEU-Silicide Targets

Substitution of uranium silicides for the uranium-aluminum alloy or uranium aluminide dispersed fuel used in other current target designs will allow the substitution of LEU for HEU in these targets with equivalent ^{99}Mo -yield per target and no change in target geometries. However, this substitution will require modifications in current processing steps due to (1) the insolubility of uranium silicides in alkaline solutions and (2) the presence of significant quantities of silicate in solution. The use of hydrogen peroxide allows the dissolution of U_3Si and U_3Si_2 . Destruction of the peroxide after uranium dissolution allows the precipitation of uranium and its separation from molybdenum. Precipitation of gelatinous silica may be avoided by maintaining the silicate concentration at or below 0.1M in the acidified dissolver solution. Under these conditions, Mo separation by alumina will be satisfactory. With these modifications, it is likely that yield and purity of the ^{99}Mo from the processing of LEU-silicide targets will not vary significantly from those of current processing of HEU targets.

ACKNOWLEDGEMENTS

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PRODUCTION OF FISSION ^{99}Mo , ^{131}I AND ^{133}Xe

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Abstract

The paper describes in general the production programmes of ^{99}Mo , ^{131}I and ^{133}Xe at IRE by irradiating and reprocessing uranium targets. Given are technical data regarding the target technology, reactor and neutron flux requirements as well as the transport of irradiated targets.

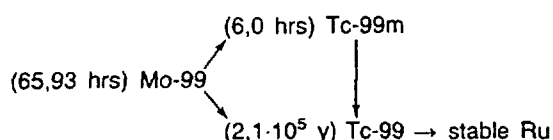
Different reactors are used for the irradiation of IRE's targets so that the different irradiation devices have been adapted to encounter the various conditions of the reactor characteristics and to obtain the desired activity by loading and unloading the targets independently of the reactor operation.

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1. INTRODUCTION

Radiopharmaceuticals have been increasingly used for the last thirty years due to the growth of nuclear medicine. Simultaneously a wide range of short lived radioisotopes has been developed. Among these radioisotopes, Tc-99m ($t_{1/2} = 6,0$ hrs) stands out from the rest because of its multiple applications (ref. 1). In addition to its rapid decay, this element has the advantage of possessing a radiation of 140 keV, easily detectable, and it allows the labelling of a large number of usable molecules for the *in vivo* tracing of the organism.

Tc-99m is produced by the decay of Mo-99, according to the following diagram.



Commercialization is generally made in the form of the Mo-99/Tc-99m generator. It essentially consists in a shielded alumina column loaded with Mo-99 from which customers can extract Tc-99m by elution with 9 % w/v NaCl.

The Tc-99m being regenerated by Mo-99 decay, the user can repeat the operation at regular intervals and prepare several times basic tracer solutions of pertechnetate.

Radiopharmaceutical utilization of generator eluates makes it necessary to use a Mo-99 with very high radionuclidic purity. Moreover, to meet present radiodiagnostic requirements, eluates with a volumic activity up to 300 mCi/ml must be obtained. This performance cannot be reached unless the generator is loaded with high specific activity Mo-99.

The Mo-98 (n, γ) Mo-99 production method, which does not make it possible to meet this demand was progressively replaced by the reprocessing of irradiated U-235. According to this method, U-235 is fissioned by bombarding it with thermal neutrons. Fission provokes the appearance of approximately 300 different isotopes which form along some 90 decay chains. Radioactive molybdenum can be recovered from the mixture of fission products.

As early as 1973, the I.R.E. studied a process for producing ^{99}Mo which allows simultaneous production of I-131 ($t_{1/2} = 8,05$ days) and Xe-133 ($t_{1/2} = 5,24$ days), two other isotopes with medical applications.

Fig. 1: Chronology of ^{99}Mo programme

	Site of the production plant	1973	1974	1975	1976	1977	1978	1979	1980	1981	1982
Elaboration of I.R.E. process	Mol - Fleurus	Mol ————— Fleurus —————									
Experimental production 30 Ci/week	Mol	—————									
Commercial production 150 to 600 Ci/week	Fleurus	—————									
Operational phase of irradiations (==>)											
at BR2		—————==>									
at HFR		—————==>									
at SILOE		—————==>									
at OSIRIS		—————==>									

This article situates the general framework in which this programme was approached and developed up to this day.

The more specific problems inherent to irradiations and reprocessing are presented in five successive articles (ref. 2 to 6).

BR2 (Mol, Belgium) and HFR (Petten, The Netherlands) were used as production reactors as soon as the programme was started. In 1979 and 1981, the devices at the SILOE (Grenoble, France) and OSIRIS (Saclay, France) reactors were put into operation, enabling the rhythm of production to be progressively increased.

2. HISTORICAL BACKGROUND

The major steps of the programme are presented in Fig. 1. As can be seen, reprocessing activities were set up in successive phases first in Mol (experimental phase) where the process was elaborated and operated at the level of 30 to 50 Ci/week, then in Fleurus (commercial phase) where a chain of cells particularly adapted for the process were installed (see Fig. 2). In this phase, production was progressively increased from 100 to 600 Ci/week.



Fig. 2: View of the I.R.E. ^{99}Mo production plant

3. MAIN TECHNICAL CONSTRAINTS

Irradiation and reprocessing of uranium to produce radioisotopes with short half-lives raises many difficulties (ref. 2 to 6).

In the following paragraphs we give a general description of the constraints encountered at the various levels.

Reactors

In order to maximise the produced activities, it is necessary to use highly enriched U-235 and to irradiate the targets in high fluxes (up to $2.5 \times 10^{14} \text{ n/cm}^2 \times \text{sec}$) so that a high rate of fission is attained. This means that the device must be designed so as to allow evacuation of heat flux reaching 250 Watts per cm^2 of cooling surface.

From the beginning, the I.R.E. programme was designed to use the possibilities of irradiation offered by BR2.

For safety reasons, the targets had to meet strictly the specification of the reactor fuel. This restriction oriented the design once and for all. The tubular form (see Fig. 3) was kept so that it would be possible to cool both sides (internal and external) and guarantee high production output.

The original targets contained 0.5 g of uranium-235. This load was subsequently increased to 4 g.

Since the routine start-up at Fleurus, the targets used correspond to the following characteristics.

- external diameter : 22.0 mm
- internal diameter : 19.46 mm
- wall thickness : 1.27 mm
- length : 160 mm
- U contained : 4 g
- enrichment : 89 to 93 %
- U concentration : 50.22 mg/cm^2

They are generally exposed to fluxes of $1.5 \times 10^{14} \text{ n/cm}^2 \times \text{sec}$ for 120 hours. In these conditions, productions of 50 Ci^{99}Mo per target can be reached 8 days after removal from the flux.

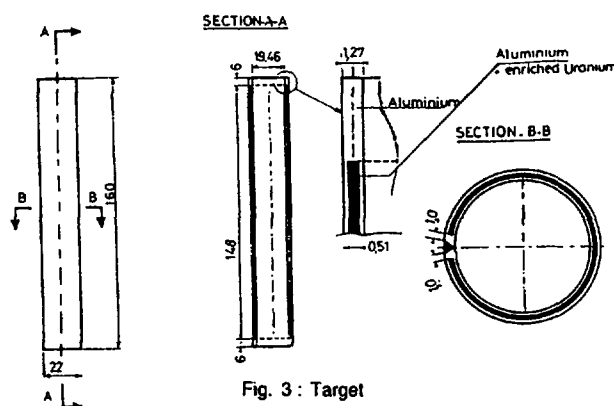


Fig. 3: Target

The low curve ray cylindrical geometry which was adapted to the irradiation conditions in the BR2 reactor required a special adjustment by the manufacturers NUKEM (Hanau, FRG) and CERCA (Romans, France). At the end of 1984, over 2.500 targets had been irradiated without any problems occurring.

Shipment

In order to reduce losses of Mo-99 through decay, the time interval between the end of irradiation and the beginning of reprocessing must be reduced to a minimum.

Cooling for a few hours directly after removal of the targets from the flux is nevertheless required to allow a drop in the dose level and in the level of heat resulting from β/γ emissions by short-lived fission products.

Shipping the targets between the reactors and the I.R.E. is ensured by lorry. This made it necessary to design an approved B(U) type special container which complied with IAEA, IATA, ADR, OMCI ... norms (see Fig. 4).

These norms require that the container is capable of withstanding exceptional transportation circumstances which are simulated in several tests :

- 1 meter drop, on a pike;
- drop on a flat surface from a height of 9 m;
- exposure to an 800°C fire for ½ hour;
- immersion in water under a pressure of 1.5 kg/cm².

At the present stage, operating conditions of the container are :

- acceptable residual heat flux : 190 Watts/target;
- activity per target : 33,000 Ci/target;
- maximum amount of targets : 3;
- weight of U-235 normally transported : 12 g.

The container's main characteristics appear in Fig. 5.

Reprocessing

This operation consists in extracting 3 isotopes Mo-99, I-131 and Xe-133 from a mixture of fission products containing some 300 radioisotopes. Because this manipulation must be accomplished with a short cooling time, activities of several tens of thousands of Curies must be manipulated.

The first phase of the programme consisted in designing and testing the process. The study of the installation was made to solve the problems inherent in shielding, ventilation, evacuation of solid and liquid wastes, storage and management of the uranium to be recovered, ...

The present state of the reprocessing technique will be discussed in the article (ref. 6) which will describe the principal options chosen to solve the technological and chemical problems encountered.

4. OPERATING CYCLE

The production cycle is represented in the following table (Fig. 6). In an outline, the goal of the programme which links reactors and I.R.E. is to put at the customer's disposal, 164 hours after the beginning of irradiation, the Mo-99 activity necessary in the manufacturing of generators. Recoveries of Xe-133 and I-131 are not sources of severe operating constraints. The produced activities largely exceed demand.

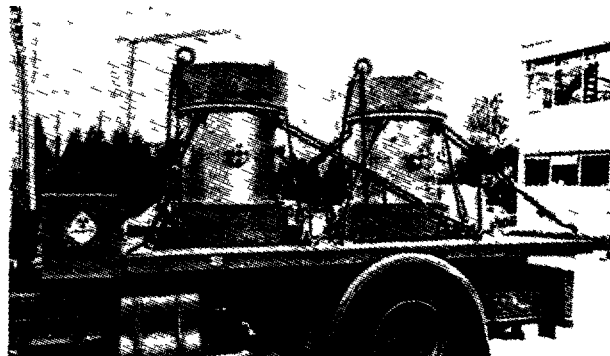
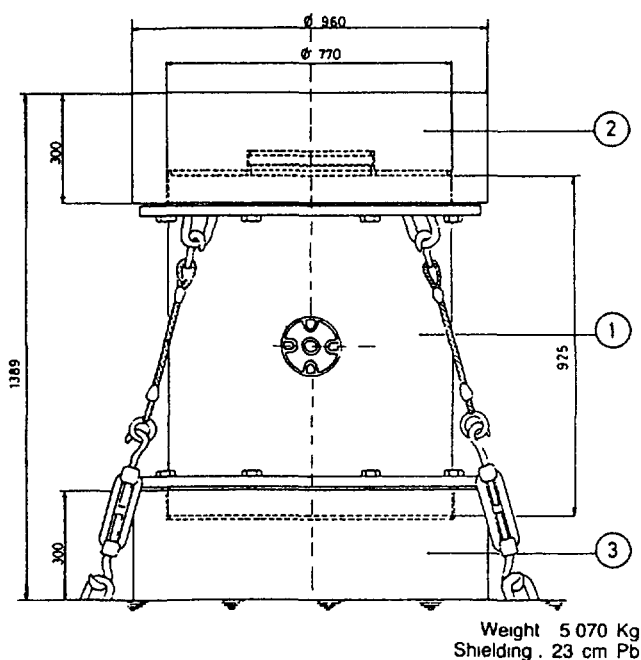


Fig. 4 . Transport of irradiated fuel targets



- 1 Body
- 2 Upper protection cover
- 3 Lower protection cover

Fig 5 Shipment container for IRE targets

	H	T	M	T	F	S	S	M	W	T	F	S	S	M	W	T	F	S	C
Irradiation																			
Shipment of irradiated targets																			
⁹⁹ Mo Production																			
^{99m} Tc Generator fabrication																			
Irradiation																			
Shipment of irradiated targets																			
⁹⁹ Mo Production																			
^{99m} Tc Generator fabrication																			
Irradiation																			
Shipment of irradiated targets																			
⁹⁹ Mo Production																			
^{99m} Tc Generator fabrication																			

Fig. 6 . Production cycle

The need to comply to a strict timetable and to ensure a reliable weekly production of Mo-99, makes it necessary to use several reactors between which there exists a desire for coordination. Should an unplanned shut-down of one of the reactors occur, it may be urgently necessary to modify irradiation and shipping schedules. A steady relation must thus be established with the transporters and the public authorities empowered to deliver transfer permits (ministries and customs).

5. CONCLUSION

The program of reprocessing irradiated U-235 implemented by I.R.E., has been described in general terms. The various problems linked to this programme have been briefly presented. More technical information is given in ref 2 to 6.

The production of fission isotopes is of major economic concern for I.R.E. This programme ensures the supply of raw materials for several radiopharmaceutical products: Tc-99m generators, Xe-133 as gaseous samples or injectable solutions, I-131 oral or intravenous solutions and capsules, various labelled molecules. Extremely severe criteria for purity must thus be satisfied for each one of these products from a radionuclidic as well as radiochemical point of view.

Reliability of production both quantitatively and qualitatively is imperative. Several years of routine operation have demonstrated that this objective has been reached.

The solutions found and the reliability of the operation are the result of close collaboration between the reactors and the Institut des Radioéléments.

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IRRADIATION OF ^{235}U IN THE OSIRIS REACTOR FOR THE PRODUCTION OF ^{99}Mo , ^{131}I AND ^{133}Xe RADIOISOTOPES

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Abstract

The irradiation device is centered in a beryllium plug with a height roughly equal to that of the core.

By using a target holder system, 3 targets can be placed in the irradiation site with a water circulation at a rate of approximately 7 m s^{-1} .

The handling is completely done under water as well as for loading and unloading into the shipping container.

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1. GENERAL CHARACTERISTICS OF THE OSIRIS REACTOR

The OSIRIS reactor is a pool type reactor. It has an installed thermal capacity of 70 MW. The reactor operates for 28 days periods which are followed by 7 days shut-downs. This regular succession of cycles goes on until summer time, period during which the reactor is shut down for a duration of approximately one month and a half.

Fuel elements are made in the form of plates which contain slightly enriched uranium oxide, of the «CARAMEL» type.

The coolant medium, which also serves as a moderator, is demineralized water, circulating in an upward direction. There are two primary coolant circuits:

- one for the reactor core,
- and one for the pool, with an entry-exit pressure difference ten times lower than for the first circuit.

The average pressure and temperature conditions of the water in the reactor core are 2.5 absolute bars and 55° Celsius respectively.

A layer of water with a temperature higher than the ambient temperature is located a few meters below the water surface: it's the «hot layer».

There are usually considered to be three main zones, for the sites chosen for experiments (see also Fig. 1):

Zone	Unperturbed thermal flux ($\text{n} \times \text{cm}^{-2} \text{s}^{-1}$)
I — Centre core	2×10^{14}
II — Peripheral core	1.5×10^{14}
III — Pool	1 to 2.5×10^{14}

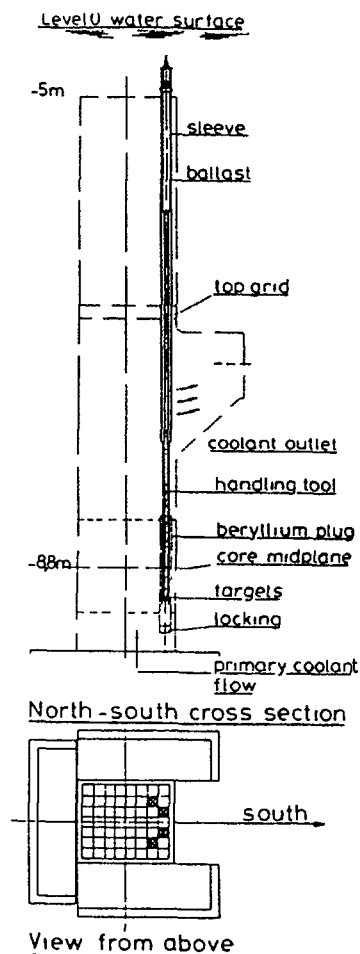


Fig. 1 Location of devices in the reactor core

The active height of the core is approximately 600 mm and the useful sections of the compartments are 84×84 mm squares.

2. GENERAL CHARACTERISTICS OF TARGETS IRRADIATION DEVICES

2.1. Positions used

They are located in zone II. The qualified sites which are currently in use, are indicated with crosses in figure 1. The targets are thus cooled by the flow of the primary coolant circuit and benefit from the reactor's clad failure detection system.

2.2. Concise description

Each device is centred in a beryllium plug (1) whose height is roughly equal to that of the core. An interlock system (anti-fly-off) is placed at the lower end.

A sleeve is centred in the beryllium plug and in the top grid (3) of the reactor. It has slots for restoration of the primary coolant flow and stops approximately 4.80 meters below the free surface of the pool. The role of this sleeve is to guide the entire target-holder system when irradiation occurs and when the targets are removed.

The target-holder system is composed of :

- a handling tool (4);
- a target holder (5) which can take 3 targets and which is locked on the handling tool.

The targets are piled on top of one another, the median target being adjusted axially in the maximum flux plane. Fins ensure the radial centering of targets on the target holder; other fins ensure the radial centering of target holders in the sleeve (see Fig. 3).

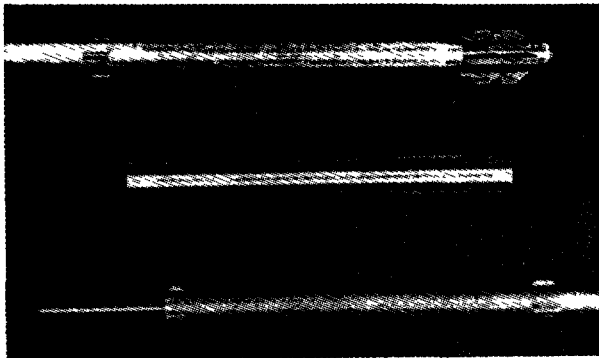


Fig. 3 : Fuel targets

The device is designed to ensure water circulation at a rate of approximately 7 m.s^{-1} and the extraction without boiling of a thermal flux of 3.000 W.cm^{-1} .

When the device does not contain any targets, a plug is set in the sleeve in order to limit the flow in the cell and avoid disturbances which would decrease the efficiency of the hot layer.

3. QUALIFICATION OF THE DEVICES

Once the irradiation site has been chosen and a geometry fixed, the qualification takes place in two steps :

- when designing, a first series of neutronic calculations enables evaluation of the effects in reactivity and power, both in the device and on the fuel elements of the core. A second series of thermohydraulic calculations makes it possible to establish the operating range of the device in relation to various constraints, the main constraint requiring that clad temperature is below water boiling temperature. These calculations are made for the permanent state of irradiation as well as for the normal transients (removal of irradiation, ...) and accidental transients (shut-down of primary circuit pumps, reactor power excursion, ...). Moreover, the calculations take into account the most unfavourable limits of the various manufacturing tolerances (dimensional tolerance of targets, target holder, sleeve, tolerance of charge of targets, ...);
- after manufacturing, tests carried out on a hydraulic test bench reproducing the characteristics of the reactor allow verification of the proper mechanic operating of the devices, the hydraulic behaviour (vibrations, fly-off, distribution of coolant flows, ...).

Thus, each device has a technical file which is checked, during its elaboration, by a permanent Commission of specialists and which is finally submitted to an examination by the nuclear safety organism of the C.E.A.

4. HANDLING UNDER WATER

This paragraph's aim is to describe the operations carried out during a production cycle : in the OSIRIS reactor, all handling is done under water, and the various necessary accessories are implanted or stored in a channel.

After the targets are removed from the fuel storage area, they are brought alongside the channel. Thanks to a handling tool, a target holder is then chosen from its storage rack and transferred to a loading platform where it is put in position. A second handling tool enables putting the targets on the target holder one at a time. The handling tool (Fig 2.) is then connected and verification is made, by exerting an axial effort, to see that it is solidly attached to the target holder. All the elements are then transferred to the reactor core and take the place of the plug of the chosen irradiation device. After the period of irradiation, approximately 5 days, the targets are removed with a travelling crane. The sleeve is sealed off again with the shutter, and the target-holder system is transferred away from the core in order to allow the power of the targets to decrease for about ten hours. The system is then secured to a rail guided cart and directed to the loading area of the containers, located at the end of the channel. An AGNES container has been prepared (its protective covers have been removed, ...). It is submerged, but remains suspended from a travelling crane. After the handling tool and target holder have been dissociated, the targets are removed one by one with a handling tool and placed in the container. The latter is then emerged and emptied of its water simply by turning it over. It is then dried, raised up, checked (leak tightness test) and loaded on the transportation carrier.

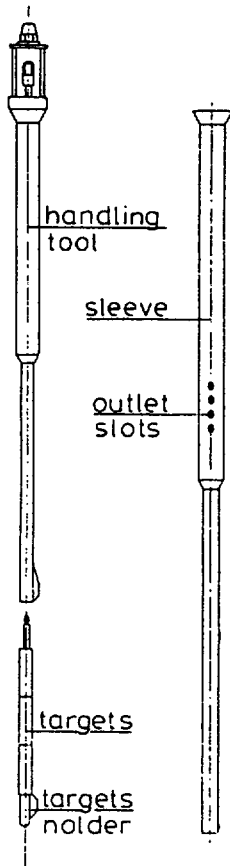


Fig. 2 : Exploded view of the device.

Introducing and removing targets is carried out when the reactor is operating, and the monitoring of operations is realized mainly with the reactor's radioprotection system. During the most critical phase, which is the loading phase into the container, a representative from the Service of Radiation Protection is present to make sure that operations progress according to the standard procedure.

5. PRODUCTION CHECK

Gamma measurements were taken, to better evaluate the power dissipated by the targets as well as to obtain a correlation with the production estimate made at the time of treatment.

The gammametric examinations were included in the normal production cycle, without disturbing it; they were carried out during the cooling periods (about 10 hours) before placing the targets in the container.

Theoretical and experimental evaluations of the molybdenum activity produced have shown the good agreement of these two methods (better than 90 %). Analyses on longer-lived radioactive elements will be undertaken in view of completing the evaluations.

6. CONCLUSIONS

The OSIRIS reactor with its usual reliability successfully irradiated fuel targets within the framework of the ^{99}Mo program of I.R.E.

The level and quality of productions increased regularly to comply with the I.R.E.'s desires. Thus 200 targets were irradiated in 1984, and an approximate weekly average of 300 Ci of molybdenum 99 were supplied calibrated 8 days after removal from the reactor.

IRRADIATION OF ^{235}U AT THE BR2 REACTOR FOR THE PRODUCTION OF ^{99}Mo , ^{131}I AND ^{133}Xe RADIOISOTOPES

Short presentation of the DGR loop

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Abstract

A special loop, called the DGR, has been studied to allow the heat evacuation by pressurized water. The in-pile section of this loop consists of a thimble tube hermetically sealed with respect to the reactor primary circuit. Two in-pile sections can irradiate simultaneously 6 targets.

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1. INTRODUCTION

This paper gives a short presentation of the BR2 reactor and the DGR loop. The DGR facility is used for irradiating samples from I.R.E., for the production of fission radioisotopes.

2. THE BR2 MATERIALS TESTING REACTOR

2.1. *Brief description and special features*

The BR2 reactor is a high-flux materials testing reactor of the thermal heterogeneous type. The fuel is 93 % ^{235}U enriched uranium in the form of plates clad in aluminium. The moderator consists of beryllium and light water, the water being pressurized (12.5 bar) and acting also as a coolant. The pressure vessel is of aluminium, and is placed in a pool of demineralized water.

One should stress the following main features of the design :

- the experimental channels are skew, the tube bundle presenting the form of a hyperboloid of revolution (see Fig. 1). This gives easy access at the top and bottom reactor covers allowing complex instrumented devices, while maintaining a very high neutron flux in the core;
- great flexibility of utilization, due to the fact that it is possible to adapt the core configuration to the experimental loading as the fissile charge can be centred on different experimental channels (Fig. 2 shows one of the recent typical core configurations used);
- although BR2 is a thermal reactor, it is possible to achieve neutron spectra very similar to those obtained

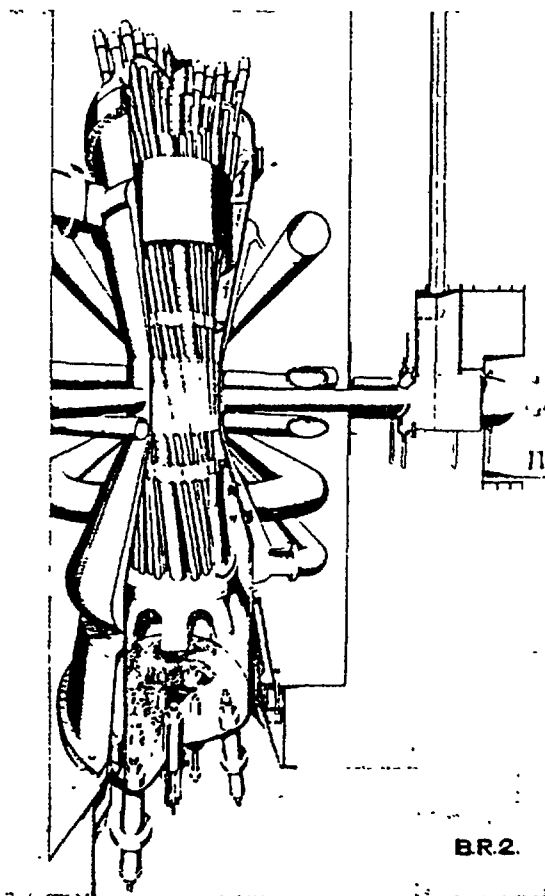


Fig 1 General view of the BR2 reactor.

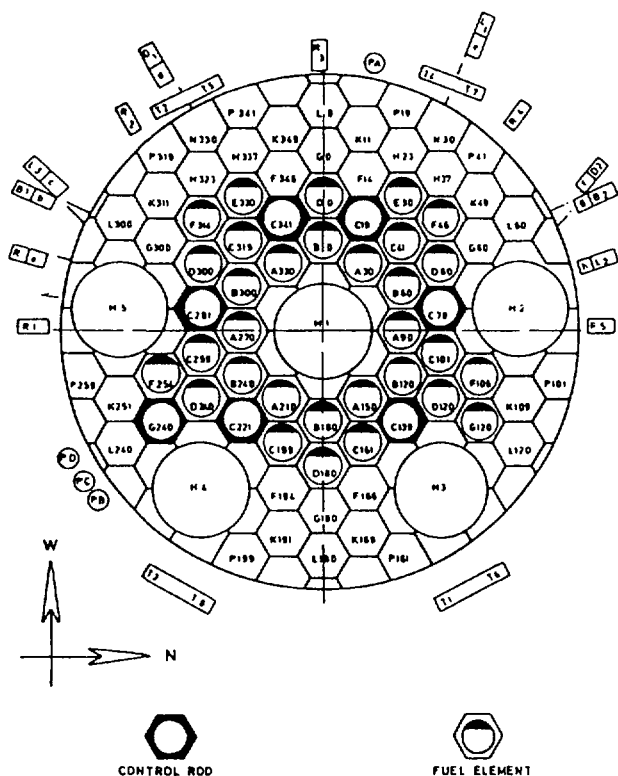


Fig. 2 : BR2 configuration 10 D.

in other reactor types, e.g. fast reactors, either by the use of absorbing screens or by the use of fissile material within the experimental device. The neutron spectrum can be «tailored»;

- besides the standard channels (84 mm diameter), five 200 mm diameter channels are available for loading large experimental irradiation devices, such as in-pile sodium, gas or water loops.

2.2. Operating characteristics

BR2 was put into service with an experimental loading in 1963. The nominal full power level depends on the core configuration; presently, it ranges from 55 to 80 MW, the maximum reached being 106 MW.

The maximum neutron fluxes available are :

- total : 1.7×10^{15} n/cm²s
- thermal : 1.1×10^{15} n/cm²s
- fast ($E > 0.1$ MeV) : 8×10^{14} n/cm²s

2.3. Reactor utilization

At BR2, a total of 100 irradiation positions are available in the core, the reflector and outside the pressure vessel (beam-tubes, reactor pool).

Purpose of the irradiations :

- study of the behaviour of fuel elements and structural materials intended for the reactors of future nuclear

power stations (sodium or gas cooled fast reactors, high temperature gas cooled reactors, light water reactors, fusion reactors);

- safety in-pile experiments (particularly related to fuel pin cooling and transient overpower) for these reactors;
- production of high specific activity radioisotopes;
- basic physical research within the beam-tubes;
- neutron-radiography in the reactor pool;
- gamma irradiations within spent fuel elements (5×10^7 rad/h or 140 W/kg).

In addition to the irradiation itself, the BR2 Operating Group can provide a complete high flux irradiation service from the planning stage all the way to the interpretation of the final results :

- assistance in the design of experimental devices;
- design and fabrication of irradiation equipment :
 - high performance loops
 - capsules for fissile and non-fissile materials, at high temperatures and high power ratings
 - retractable and reloadable devices
 - tests on pre-irradiated fuel pins
 - power cycling devices
 - capsules for isotopes and transplutonium elements production;
- testing and commissioning of irradiation equipment;
- dosimetric analysis :
 - determination of optimum irradiation conditions with experimental mockups in the zero power reactor BR02
 - thermal and fast neutron detectors measurements;
- post-irradiation examinations and analysis :
 - dismantling of equipment
 - standard metallurgical and physical tests in hot cells
 - chemical operations and analysis.

3. THE DGR LOOP

The BR2 reactor was previously equipped with several irradiation devices allowing loading and unloading of the samples during reactor operation.

None of these devices however could accept large samples producing a large amount of heat.

It was then decided to design a pressurized water loop with a heat evacuation capacity of about 100 kW, accepting samples with a large diameter and with a high contamination hazard.

The annexed figure presents a simplified schematic diagram of the whole loop (Fig. 3).

The in-pile section of this loop consists of a thimble tube hermetically sealed with respect to the reactor primary circuit; this tube, intended to accept the samples, is attached to the reactor cover and penetrates into the reactor core; it is connected above the reactor cover (reactor pool) to its own circulation group, allowing the cooling of the samples by forced convection; the heat removed by the coolant is

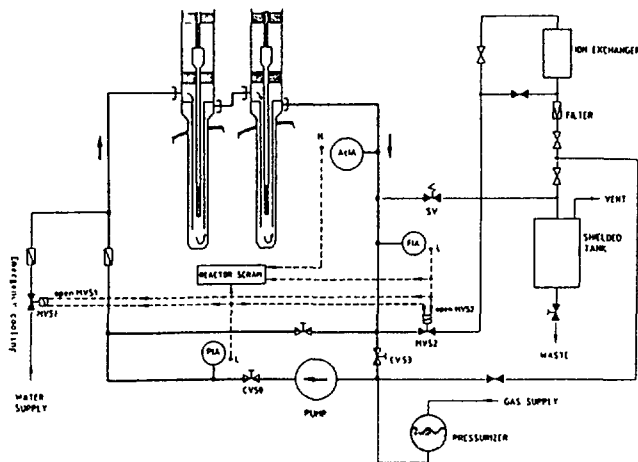


Fig.3 : DGR loop — Schematic diagram.

transferred to the reactor primary coolant through the thimble tube wall and to the reactor pool water by the rest of the circuit.

From these features comes the name «DGR», acronym for «Doigt de Gant Refroidi».

The top of this tube can be remotely opened and closed in order to introduce or to unload some samples.

The samples are attached to a basket, connected to a moving piston gliding in a stuffing box located at the upper end of the thimble tube.

Introduction of the samples into the thimble occurs under water (reactor pool).

Once the samples loaded and the tube closed, the loop is pressurized and the circulation group is started. The samples are then lowered into the neutron flux by a remotely commanded screw actuating the moving piston downwards.

Unloading of the samples occurs according to the following procedure :

- the moving piston is upwards actuated, in order to withdraw the samples from the neutron flux;
- the samples are then allowed to cool for a few hours;
- the circulation group is stopped and the loop is depressurized;
- the thimble tube is opened under water, the samples are extracted and transported to a safe storage area.

The loop is provided with a purification unit in order to limit the contamination level due to an eventual sample failure.

An emergency cooling circuit starts automatically in case of pump defect.

Loop accidental depressurization, loss of coolant flow rate or a too high activity level in the loop are detected and produce an automatic reactor scram.

Since the beginning of operation at the end of 1980, the loop was used for the irradiation of targets for account of the I.R.E., in order to produce Mo-99/Xe-133/I-131 radioisotopes.

Since the thermohydraulic characteristics allowed the operation with a second in-pile section, the capacities of the loop for radioisotope production and heat removal were recently doubled by the series connection of a second thimble tube.

The following table gives a summary of the loop operational characteristics when equipped with two thimble tubes loaded with the I.R.E. targets.

DGR Loop operational characteristics

Targets dimensions : max. outer diameter	23 mm
max. length	650 mm
Number of targets for 2 in-pile sections	6
Operating pressure	up to 13 bar
Max. flow rate of coolant	6 m ³ /h
Heat evacuation capacity : nominal	220 kW
maximal	260 kW

4. CONCLUSION

Irradiation of U-235 in the BR2 reactor at the request of the I.R.E. for the production of Mo-99, Xe-133, I-131 started in 1975, the definition of the main characteristics of this new I.R.E. programme having been based on the BR2 irradiation possibilities.

Since that time, the irradiation capacity has been regularly adapted to the evolution of the demands.

Presently, irradiation of U-235 occurs routinely at a rate of 3 campaigns per BR2 operating cycle of one month, a campaign involving the irradiation of up to 6 targets.

IRRADIATION OF ^{235}U IN THE HFR PETTEN FOR THE PRODUCTION OF ^{99}Mo , ^{131}I AND ^{133}Xe RADIOISOTOPES

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Abstract

The irradiation can take place in the PSF (Pool Side Facility) or in a special in-core facility called TRIO-FIT.

In the PSF, two positions with high neutron beams allow to irradiate 6 targets whereas the TRIO-FIT accepts 9 targets in three parallel channels, simultaneously.

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1. THE HIGH FLUX REACTOR, PETTEN

The Petten Establishment is one of the four establishments of the Joint Research Centre (JRC) of the Commission of the European Communities. The High Flux Reactor (HFR) (ref. 1) of the JRC Petten is operated to perform irradiation experiments in cooperation with different research teams to support research and development in the fields of :

- nuclear fusion energy, especially safety features;
- thermonuclear fusion, study of potential materials to be used in controlled fusion reactors;
- solid state and nuclear structure physics, fundamental research with neutron beams and additional equipment;
- production of radioisotopes for medical, industrial and agricultural applications (ref. 2);
- to perform neutron activation analyses for geological and environmental studies.

The HFR is a multipurpose materials testing reactor using highly enriched uranium plate type fuel elements with burnable poison, light water coolant moderator and a beryllium moderator reflector.

The HFR operates at 45 MW for about 285 days per annum. The core lattice is a 9×9 array containing usually 33 fuel elements, 6 control rods, 25 beryllium elements and 17 experiment positions with aluminium filler elements (see Fig. 1). Reactor primary cooling is provided by recirculating 4.100 m³h demineralised water through the reactor vessel at a pressure of 3.4 bar and a temperature of 313 K at the core inlet. The water level in the reactor pool is usually 8.7 m, this is 4.3 m above the reactor vessel. Adjacent to the reactor pool there are two smaller pools for storage and handling radioactive objects. On top of one of

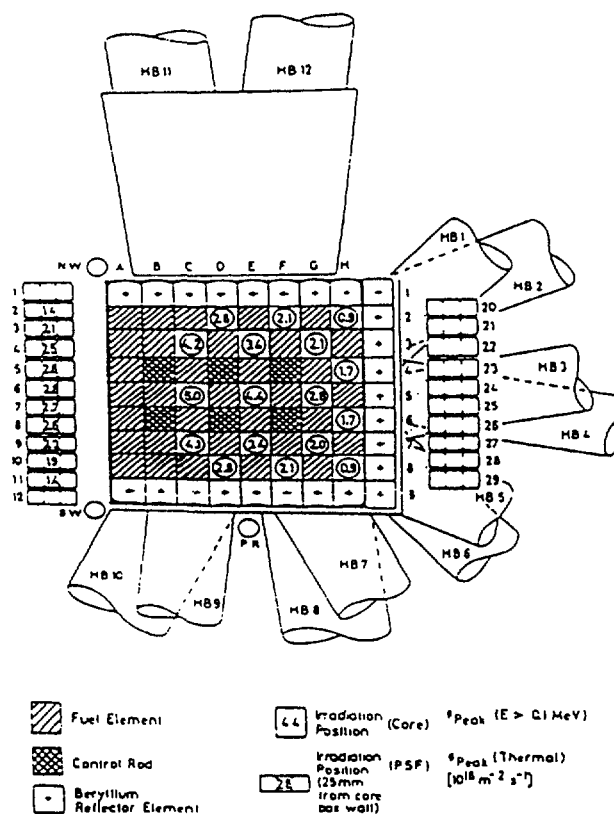


Fig. 1 : NEW HFR CORE CONFIGURATION AND BEAM TUBES

them there is a hot cell for the dismantling of irradiation devices.

Besides the 17 in-core experiment positions with straight access, there are 20 irradiation positions in the Pool Side Facility (PSF) outside the vessel, and 11 horizontal beam tubes. Neutron fluence rates vary from $3.3 \times 10^{18} \text{m}^{-2}\text{s}^{-1}$ thermal in the PSF to 4.4 fast in the core centre. The reactor pressure vessel, having been in service for more than 20 years, was replaced in 1984 by a new vessel, which provides even better access to core and PSF experiment positions and allows a second PSF.

Radioisotope production in HFR takes place in standardized carriers in both in-core experiment positions and in the irradiation positions in the PSF. On the average, about 15 % of the reactor capacity is used for the production of radioisotopes (ref. 3).

2. THE IRRADIATION STORY OF I.R.E. ^{235}U TARGETS IN THE HFR

A first contact was made in 1974 between I.R.E. and J.R.C. concerning the irradiation of ^{235}U with an enrichment of 93 % and 16 mm diameter targets. In February 1976, a first test irradiation in the Pool Side Facility took place. In order to determine exactly the flux density, an Ag-collector has been mounted on a special device fixed on the rack. Other tests were carried out concerning handling and transport of the irradiated targets. In May 1976, the production irradiations started. Until September 1979, a total of 76 irradiations (228 targets) with 16 mm diameter targets were carried out and transported to I.R.E. Mol or Fleurus.

To increase the nuclear power to 20 kW, an increase of both fission rate and ^{235}U target contents was necessary. To respond to this request, a new capsule for an in-core application (see 3) was developed, allowing the irradiation in a core position of the HFR. The first 22 mm diameter targets irradiation took place in a modified PSF capsule in March 1980. The in-core capsule was ready in May 1980. Until November 1983, date when the HFR was shut down for the vessel replacement, 147 irradiations (441 targets) in PSF and in-core positions were carried out.

3. CHARACTERISTICS OF THE IRRADIATION DEVICES

In order to guarantee a regular production service, several irradiation devices are available at the HFR Petten for PSF positions and in-core positions.

The latter is described in some detail because it presents interesting technical features :

- efficient cooling of the fissile specimens is provided by the reactor primary cooling circuit;
- the risk of fission products release requires a sealed cooling circuit which is provided by the reactor vessel and circuitry;
- prompt loading and unloading of the targets;
- increase of the fission rate.

These four items have determined the development of the irradiation device TRIO-FIT (see Fig. 2) which allows irradiation of 9 targets in three parallel channels, simultaneously. Through a system of three sluiceways, (ref. 4) the loading and unloading of the targets can be realized, without interrupting the reactor operation, i.e. without inter-

rupting the primary cooling of the reactor or the cooling of the targets.

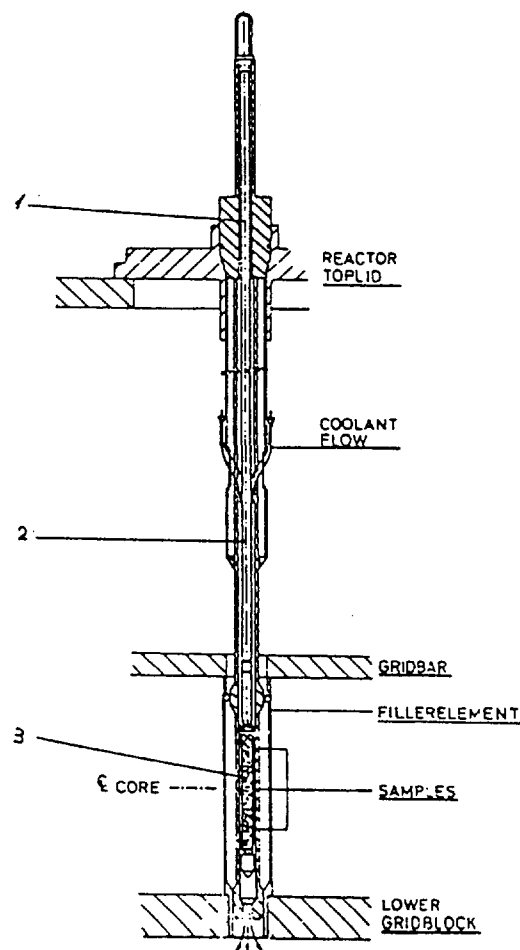


Fig. 2 : Irradiation facility

4. CONCLUSIONS

The reactor predictable operation schedule and performance of the reactor, together with the perfectly organized in-pool handling and road transport, have yielded more than 200 successful irradiations on behalf of I.R.E. Fleurus.

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IRRADIATION OF ^{235}U IN THE SILOE REACTOR FOR THE PRODUCTION OF ^{99}Mo , ^{131}I AND ^{133}Xe RADIOISOTOPES

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Abstract

The irradiation device occupies a position located in the peripheral area of the reactor core behind the beryllium reflector.

This facility can contain 12 targets and consists of a coolant guide and four target holders.

The targets are unloaded into a hot cell with a hermetic connection with the special shipping container.

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1. THE SILOE REACTOR (Fig. 1)



Fig. 1

1.1. Characteristics

- Open core pool-type reactor
- Power : 35 MW
- Neutron reflector : water and beryllium
- Available fluxes : thermal neutrons : 1 to 3.10^{14} neutrons. $\text{cm}^{-2}.\text{sec}^{-1}$.

1.2. Experimental facilities

- Direct access to the core from the pool
- Irradiation locations with high neutron fluxes in the core
- Form of core adaptable to specific experiences
- Movable rig holders allowing continual variation of the neutron fluxes (water box)
- Possibility of centring lengthy irradiation devices in relation to the core.

1.3. Irradiation devices

They are the tools necessary for irradiating structure materials and fuels from electronuclear power plants in conditions representative of reactor systems. Two categories of instruments devices are used :

- the *loops* in which calorific power is extracted by a coolant in forced convection :
 - heat pump : sodium loop for cladding failures studies on fuel pins;
 - Elise : sodium loop for studying the operating limits of one or several fuel pins;
 - jet pump : pressurized water loop for the irradiation of fuel rods with failed or undamaged clad;
- the *capsules* in which calorific power is extracted by a coolant under static or natural convection :
 - chouca : capsule for the irradiation of structural materials for all reactor systems;
 - cyrano, cylex : capsules for the irradiation of fuel materials;
 - aquilon, griffon, flash : pressurized water capsules for the irradiation of fuel rods.

1.4. Connected equipment

- Hot cell : direct access to the $4.50 \times 2.00 \times 3.50$ m cell by way of an underwater channel is possible from the irradiation pool
- Gamma spectrometry : a high performing gamma scanning table submerged in the reactor's pool enables the irradiation devices to be examined

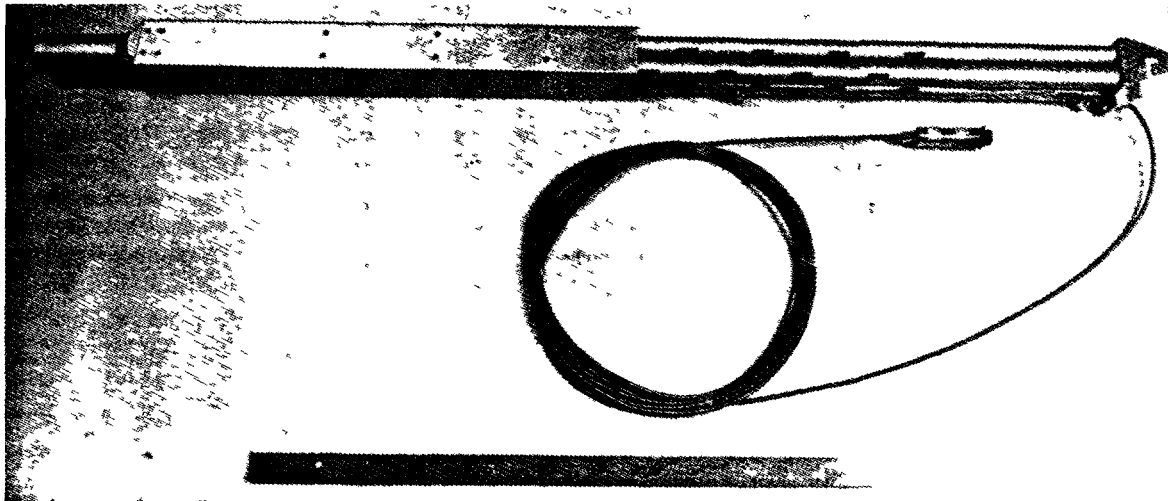


Fig. 2 Irradiation device

— Neutron radiography a submerged slotted measuring section in the main pool of the reactor enables the irradiation devices to be checked, namely those containing fuel.

1.5. Dosimetry laboratory

The dosimetry laboratory is in charge of measurement of radiation doses applied in the experiments.

1.6. Analysis laboratory for fission products

The laboratory set up at SILOE by the Department of Metallurgy of Grenoble (DMG) analyses in line the stable and radioactive isotopes emitted during the irradiations of devices containing fuel.

1.7. Utilization

- Fundamental research : the ejected neutron beams are used for studying the structure of the materials
- Research applied to the development of electronuclear reactor systems. There exist for all reactor systems — pressurized water reactors, fast neutron reactors, gas-cooled reactors, boiling water reactors, fusion reactors — irradiation sites and devices which enable tests to be performed on nuclear materials and fuels
- Production of radioactive elements : cobalt-60, iridium-192, molybdenum-99,...

2 PRODUCTION OF FISSION MOLYBDENUM

Molybdenum-99 is produced by fission of the uranium-235 contained in tubular targets loaded with 4 g of 93 % enriched uranium.

The irradiation device used in SILOE occupies a position located in the peripheral region of the core behind the beryllium reflector. Its volume which is equal to $76 \times 72 \times 700$ mm can contain a maximum of 12 targets. It includes :

2.1. A coolant guide (fig. 2 and 3) made of aluminium is composed of :

- a cylindrical base (1) which ensures the centring on the reactor grid (2) and channeling of the target coolant water flow;
- a 76×72 rectangular casing (3) which forms the framework of the four irradiation channels (4) and the stand for the detectors (5) measuring neutron fluxes;

- four tubular channels (4) into which are introduced the target holders, these channels are long enough so that during the introduction and removal of the target holders, the targets are always cooled and guided. When a channel is not occupied, a plug (12) maintains a balanced cooling flow in the adjacent channels (6);

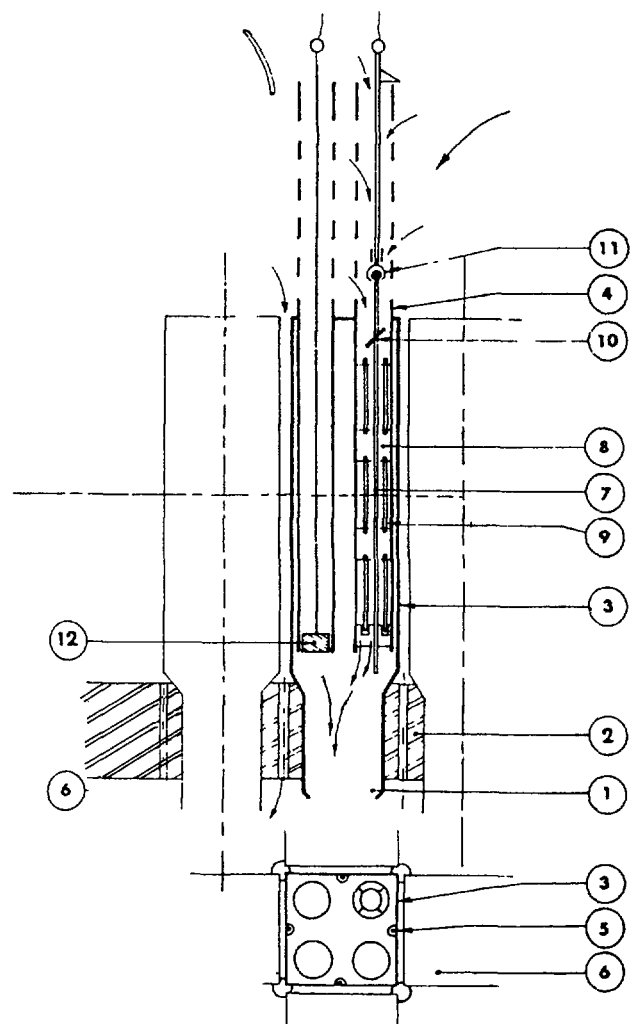


Fig 3 Irradiation facility

- four detectors used to measure neutron fluxes (5) (self power neutron detectors) which are placed between the irradiation channels. The *current* induced by the nuclear reaction on the constituent materials is *proportional to the incident neutron flux*. The processing of the collected signals makes it possible to determine the reaction rate in the targets and to know the quantity of Mo-99 produced by fission.

2.2. *Four target holders* (Fig. 3, 4 and 5)

Each aluminium target holder is composed of a stem based (7) with target holders (8) ensuring the positioning of the three targets (9) piled up in the channel.

The heat given off by uranium fission and gamma energy is evacuated to the internal and external surface of the targets by the water coolant. Surface heat flux can reach 180 W/cm².

The setting up and dismantling of targets on the target holder is carried out with a manipulator in the hot cell of SILOE.

The target holders (8) and removable targets are interlocked (10). A connection system (11) makes manipulation in the cell of the reactor easier.

3. THE PHYSICS OF THE SYSTEM

Determination of the produced molybdenum-99 is done with the information from the self power neutron detectors, calibration being carried out by means of gamma spectrometry.

3.1. *Using signals delivered by the self power neutron detectors*

In order to determine molybdenum-99 activity as well as the evacuated calorific power, it is necessary to :

- know incident neutron fluxes near targets;
- calculate the number of fissions in uranium-235;
- determine the evolution of the number of molybdenum-99 nuclei formed during irradiation.

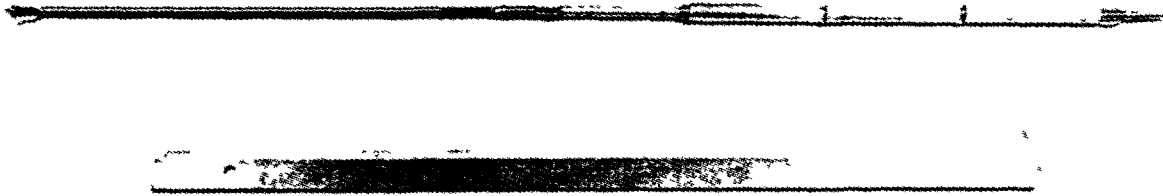


Fig. 4 : Fuel targets before irradiation

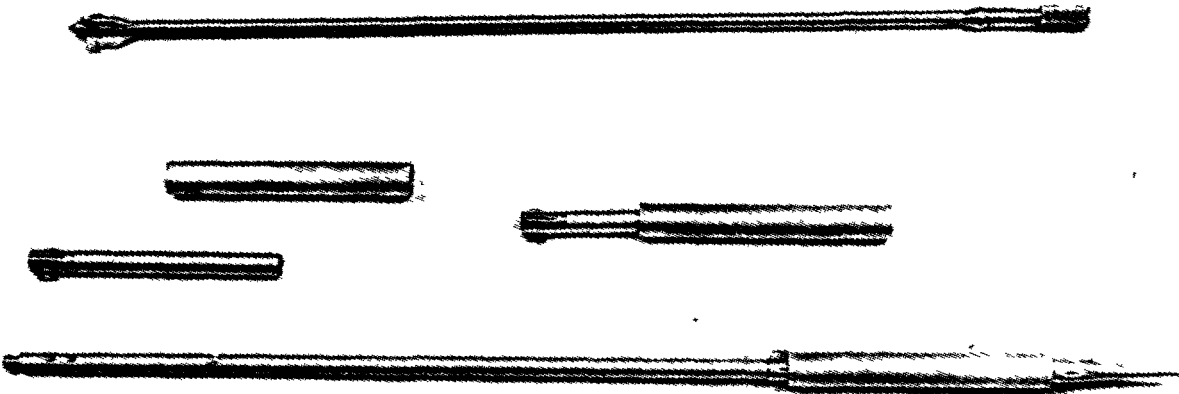


Fig. 5 : Fuel targets with target holder

3 1 1 Measurement of neutron flux

The detector currently used on all irradiation devices is a sheathed and insulated rhodium wire. After capture, the rhodium isotope 103 emits an electron.

The rhodium wire used has a diameter of 0.5 mm and a length of 50 mm. It is insulated with alumina in a stainless steel coaxial sheath. An apparatus which is connected to the detector by a coaxial line measures the electric current induced by the reconversion electrons. The current is proportional to the incident neutron fluxes.

3 1 2 Calculation of the fission rate

The calculation is done in cylindrical geometry with the help of the "APOLLO" transportation code and the "BENA-POL" auxiliary code. The following data are entered:

- incident neutronic spectrum divided into 99 energy groups,
- effective fission and uranium-235 neutron capture section.

The result is the fission rate of uranium-235 and the production rate of molybdenum-99.

3 1 3 Calculation of the evolution of molybdenum-99 activity

The calculation is made with the "EVOGE" code. It takes into account the incident neutron flux variations during irradiation and determines the balance between the fission produced quantity and the quantity that has disappeared with radioactive decay (half life = 66 hours).

3 1 4 Results

The following table gives an example of the results obtained for each target of a target holder. The molybdenum-99 activity is the one at the end of irradiation (removal from reactor).

Target Nr	10	12	11
Position	lower	median	upper
Weight of U5 (g)	3.74	3.80	3.81
Duration of irradiation (hours)	96	96	96
Mo 99 activity (Ci)	507	625	424
Average power per target ($W \times cm^{-2}$)	940	1 163	784

3 2. Utilization of examinations carried out with gamma spectrometry

3 2 1 Principle

The gamma scanning of a radioactive source makes it possible to determine qualitatively and quantitatively its isotopic composition. It is a nondestructive technique which is used during the irradiation of a device.

With this technique it is possible to study the behaviour of a fuel sample (distribution of fission products, power given off) or the elements of a device which can be contaminated by fission products (study of the cladding failure of a fuel pin).

This makes it necessary to interrupt the irradiation and to transfer the device to a slotted measuring section located in the reactor pool. The range of the radionuclides measured is very wide, with decay periods from 50 min (I-134) all the way to 30 years (Cs-137).

A complete analysis requires several examinations in order to limit the influence of radionuclides with shorter periods.

3 2.2 Examination of uranium targets

In order to qualify the results obtained with the neutron detectors, 3 targets were irradiated for 4 days at nominal conditions, then examined by means of gamma spectrometry after 3 days of radioactive decay.

Values for power and Mo-99 activity, in the following table, are deducted from the quantitative measure of certain radionuclides such as Zr-95, Mo-99, Ru-103, I-131, Te-132, Ba-140 with a medium decay period, supposing that fission products such as I and Te did not migrate in the fuel.

Target Nr	10	12	11
Position 05 AR	lower	median	upper
Weight of U5 (g)	3.74	3.80	3.81
Duration of irradiation (hours)	96	96	96
Power			
— surface ($W \times cm^{-2}$)	107	121	95
— linear ($W \times cm^{-1}$)	1 110	1 260	990
Average power on the targets linear ($W \times cm^{-1}$)	1 005	1 185	880
Average activity of Mo-99 (Ci/target)	520	610	455

Figure 6 indicates the distribution of the targets' entire activity.

_IRE Targets -August 1984
- DT = 4 days

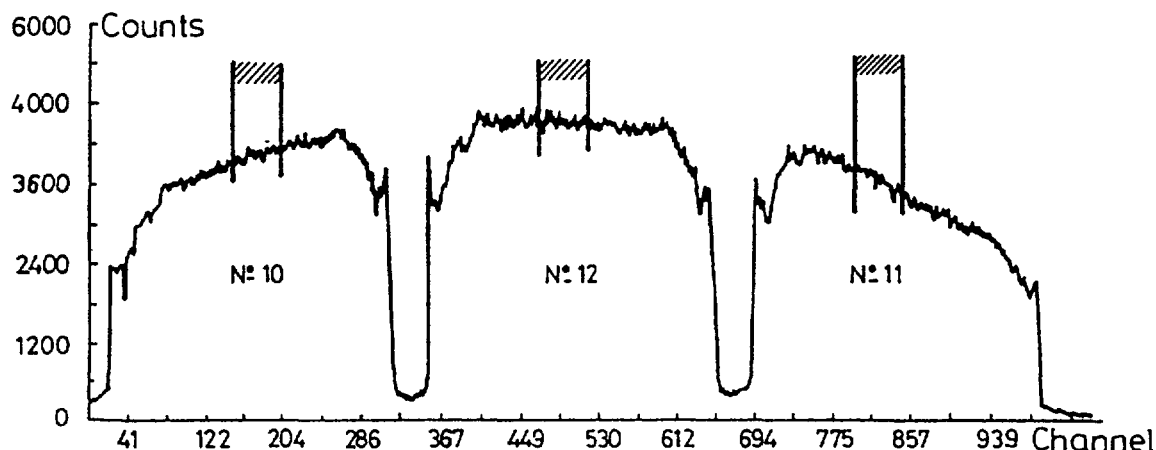


Fig. 6 : Longitudinal distribution of total activity

4. THE THERMOHYDRAULICS OF THE SYSTEM

4.1. Principle

The calculation of cooling is identical to that made for SILOE reactor fuel elements, because the criteria for thermohydraulic safety are the same.

Two types of operations are considered :

- normal operation;
- incidental operation corresponding to degraded thermohydraulic conditions just before emergency shut-down of the reactor.

The safety criteria to be remembered are :

- no local boiling at the hottest part of the targets when in normal operation;
- no redistribution of the cooling water flow to the limits of safety thresholds.

4.2. Calculation

It is made with the help of the "SILCOR" code. The data to be entered are the characteristics of the system (geometry of the channel and targets, pressure and temperature of water, power given off by the targets, etc...).

For each one of the two types of operations considered, the code determines along the cooling channel the temperature of the water and the outer surface of the targets as well as the speed.

The calculation is carried out with the nominal values of the data and also with the same values all uncertainties added together. The uncertainties involve the geometry of the channel, the content in U5 of the targets as well as the formulas used.

5. HANDLING AND TRANSPORTATION

After being irradiated, the targets are transferred to AGNES flask for shipment to the FLEURUS Institut des Radioéléments.

5.1. Unloading of targets of the target holder

The target holders are removed from the coolant guide by means of a rope and transferred while submerged in the storage bassin (1) of the reactor and then introduced by the transfer channel (2) into the hot cell, the door (4) being open.

After the door of the hot cell is closed, each target holder is removed from the water by using the winch of the hot cell. Under the effect of the residual energy, the targets are rapidly dried.

The target holder is placed on the work table (5) in the hot cell then dismantled by using manipulators to extract the three targets.

5.2. Loading of the targets in the AGNES container (Fig. 7 and 8)

With the travelling crane, the AGNES container is placed on the storage space to remove its protective covers. It is then raised by means of a handling device which allows it to sway in horizontal position.

After the front and back safety flanges are removed (8), the container (9) is placed on the cart serving as a cradle (10) in front of the opening (11) made in the wall of the hot cell (12).

The back lock of the container plug is open and the poker (13) screwed onto the target holder basket (14). The container is brought forward until it comes into contact with the sliding door (15) of the cell. By manoeuvring the poker in a rotative then translatory movement, the plugs (16) of the cask and basket are retracted into the sliding door. The sliding of this door opens the way for the target holder basket which is then introduced in the hot cell to receive the three targets (7).

The loaded targets holder basket is installed according to a series of operations which are in the reverse order of the previous ones.

The AGNES container is placed after radiation control on the transportation carrier.

All the operations combined do not even last one hour.

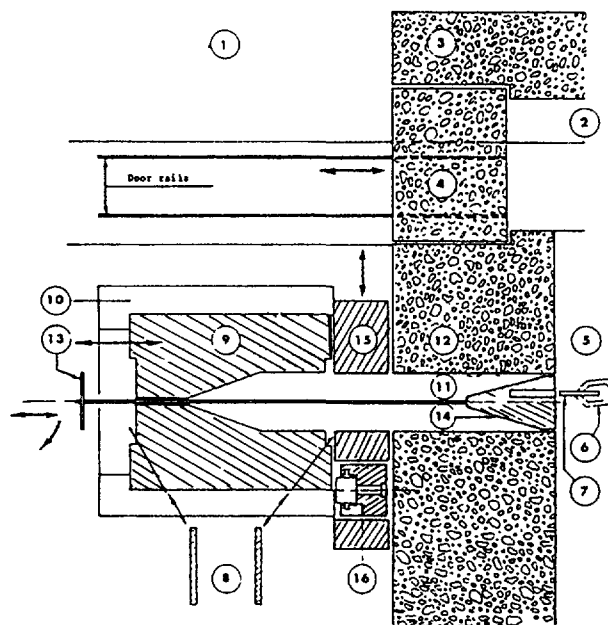


Fig. 7 . Loading of the container

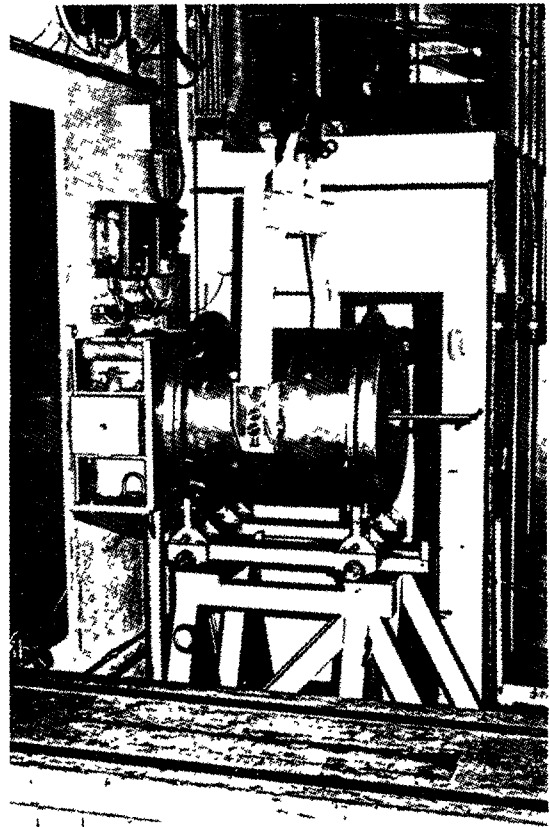


Fig. 8 : AGNES container connected on the cell

6. CONCLUSION

The SILOE reactor was used as early as 1979 with the start-up of the Mo-99 programme at Fleurus.

The main characteristics of the device have been described in the preceeding pages. In order to optimize the irradiation parameters, SILOE carried out several series of measurements whose results made it possible to improve production forecasts.

Placing the targets into containers at SILOE has the particularity of taking place outside of the pool by means of a transfer cell.

REPROCESSING OF IRRADIATED ^{235}U FOR THE PRODUCTION OF ^{99}Mo , ^{131}I AND ^{133}Xe RADIOISOTOPES

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Abstract

The plant reprocessing irradiated Uranium-235 uses 6 hot cells and two shielded boxes.

After removing the targets from the transport container, adapted to the special hot-cell door, the reprocessing follows the different steps, dissolution of targets, filtration, acidification, purification on alumina, dowex and activated carbon columns.

The routine performance of the facility is indicated as well as the radionuclidic purity as for the operation yields.

Depending on the reactor used, the obtained Mo-99 activity varies from 12 TBq to 19 TBq post calibrated 8 days after unloading 6 targets from the reactor.

Complementary, more than 20 TBq Xe-133 and 5 TBq I-131 at the same calibration date are recuperated by side-processes developed into shielded boxes (Xe-133) and a special hot cell (I-131).

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1. INTRODUCTION

the reprocessing of fissioned uranium in view of producing short-lived radio-elements involves particularly severe work constraints.

It implies the manipulation of irradiated targets in a very short time span so as to limit losses by decay of the isotope to be extracted. The reprocessed activity is of several tens of thousands of curies. The reprocessing plant must thus include heavy shielded cells, equipped with sophisticated ventilation and safety equipment systems.

Moreover, it requires a very effective process to extract with a good yield, radioisotopes presenting excellent purity characteristics, from a complex chemical mixture.

Fission is nevertheless used for the production of several radio-elements intended for medical applications, Mo-99, I-131 and Xe-133, because it allows to produce several hundred curies in one batch and obtain high specific activities.

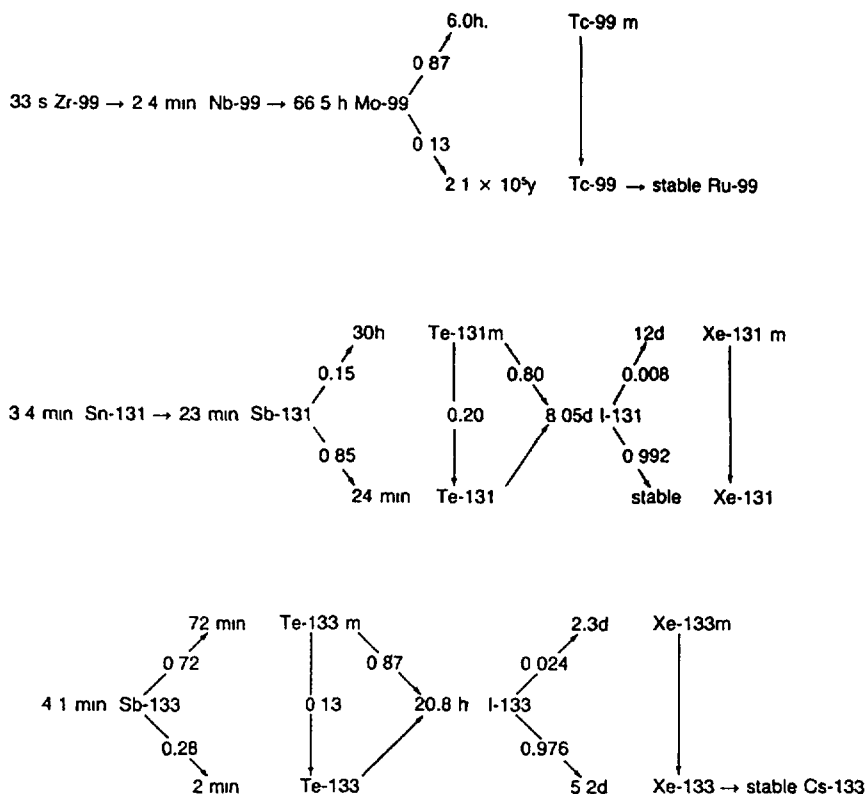
Existing literature describes several processes (ref. 1, 2 and 3) for the manufacturing of these isotopes. The technique used at the "Institut National des Radioéléments" (I.R.E.) results in the triple production of Mo-99, I-131 and Xe-133 from one single irradiation.

The aim of this article is to succinctly present the process developed and used at the I.R.E. (ref. 4).

2. PRINCIPLE OF THE PRODUCTION

When bombarded with neutrons, uranium-235 fissions into elements with a weaker mass which, themselves unstable, generate, through a decay chain, other radioisotopes.

The fission chains resulting in Mo-99, I-131 and Xe-133 are represented below (ref. 5).



At the time of formation, molybdenum, iodine and xenon are present in the form of several isotopes (see Table I).

TABLE I

Molybdenum			Iodine			Xenon		
Atomic mass	Half-life	Fission yield %(*)	Atomic mass	Half-life	Fission yield %(*)	Atomic mass	Half-life	Fission yield %(*)
95	stable	6.27	127	stable	0.13	129	stable	0.8
97	stable	6.09	129	1.7×10^7 yrs	0.8	131m	12 days	3.1
98	stable	5.78	131	8.05 days	3.1	131	stable	3.1
99	66.5 hrs	6.06	132	2.30 hrs	4.7	132	stable	4.38
100	stable	6.30	133	20.8 hrs	6.62	133m	2.3 days	6.62
101	14.6 min.	5.0	134	52.5 min	8.06	133	5.27 days	6.62
102	11.5 min.	4.3	135	6.70 hrs	6.3	134	stable	8.06
			136 to 139	a few sec to a few min		135	9.2 hrs	6.3
						136	stable	6.46
						137 to 140	a few sec. to a few min	

(*) Yields are given for the chains without considering branching ratios

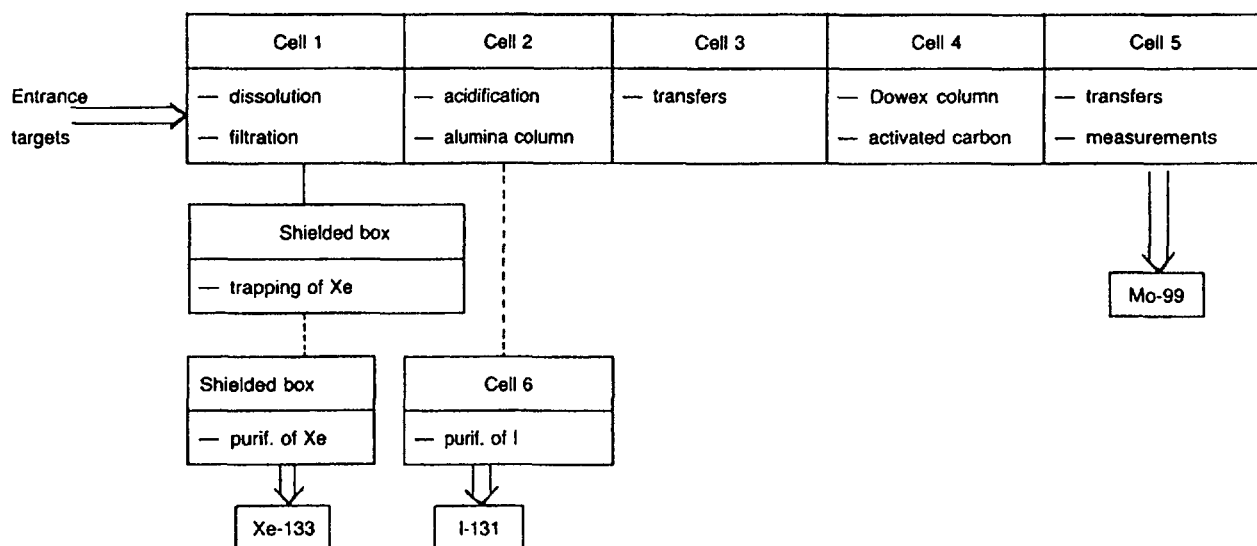
It can be seen from the table that Mo-99 will not be, at the end of production, contaminated with an isotope of short half-life. However, its specific activity will be decreased by the presence of molybdenum 97, 98 and 100.

The period of irradiation remaining short (i.e. 5 days), iodine 129 activities remain low in comparison to I-131 activities. On the other hand, high I-133 and I-135 activities will be formed

As for xenon, there will be, when purified during the week following irradiation, high Xe-135 residual activity. Beyond that, only Xe-131 m and Xe-133 m represent potential contaminants. Kr-85 is not sufficiently active to affect the product's purity.

3. DESCRIPTION OF THE PLANT

The entire reprocessing plant is described in the figure below. The use of each cell and box is indicated.



- The Mo-99 process is installed in 5 cells. Cells 3 and 5 are used to introduce cold material, extract samples for process control and load ^{99}Mo samples into containers after dispensing. An ionization chamber installed in C5 enables the control of the supplied activities. The shields are adapted to the level of manipulated activity. Thus, the cells have a lead protection of :
 - 25 cm for dissolution and filtration;
 - 20 cm for acidification and alumina chromatography;
 - 15 cm for the remainder of the process.

Certain particularly active areas are overshielded, in order to reduce irradiation inside the cells, and to comply with dose rates of 2 mRem/hour at the cells' surface.

The entire chain is equipped with a ventilation system, ensuring effective protection against the risk of an I-131 release into the environment, by filtration on active carbon.

- The shielded box containing the trapping device for xenon liberated during dissolution is coupled on this chain. Once trapped, the xenon is transferred in a separate installation, to be purified.
- The essential phases of iodine production occur in cell 2 : trapping $^{131}\text{I}_2$ during acidification and in cell 6 : desorption of I-131 and chemical purification by distillation.

4. DESCRIPTION OF THE PROCESS

4.1. Irradiation

The target's characteristics have been given (ref. 6). Each target is essentially composed of 30 g Al and 4.2 g of 89 to 93 % enriched U. The targets are irradiated and reprocessed in batches of 3 or 6 pieces.

Irradiation parameters vary according to the reactor used. On the average, the following conditions are complied to :

- duration of irradiation : 100 to 120 hours;
- undisturbed neutronic flux : 1.5 to 2.5×10^{14} n/cm² x sec.

The targets are cooled down for a few hours in the reactor pool before being placed in containers and shipped to I.R.E., Fleurus.

In practice, reprocessing commences 24 to 36 hours after irradiation.

4.2. Reprocessing

The main steps of the procedure appear in the following flow-sheet (Fig. 1).

4.2.1. Dissolution of targets

The dissolution of 3 targets takes place by means of 1.575 ml NaOH 3N - NaNO₃ 4N. This operation provokes the liberation of xenon, the dissolution of iodine-131 in the form of I⁻ and molybdenum in the form of MoO₄²⁻. The uranium and a large part of the fission products hydroxydes are precipitated simultaneously.

The released xenon is carried by helium toward the condensation traps installed in the shielded box where it is condensed on copper clippings cooled down to -196° by means of liquid nitrogen. Further down from this first trap, there is an active carbon trap installed which is also cooled, preventing discharges of xenon toward the ventilation system.

The trapped xenon is subsequently transferred in a container and shipped to a purification plant. This last step consists in chromatography on carbon. It aims at eliminating CO₂, O₂, N₂O... and concentrating the xenon.

4.2.2. Filtration

This phase consists in separating the precipitate cake in view of its subsequent reprocessing, in order to recover the unfissioned uranium.

4.2.3. Acidification

After dilution with 1.800 ml H₂O, 1.460 ml concentrated HNO₃ are added to the filtrate. The solution is shaken by means of air bubbles and heated.

The released iodine is trapped on platinum asbestos. This is then transferred to cell 6, to be reprocessed in view of recovering I-131.

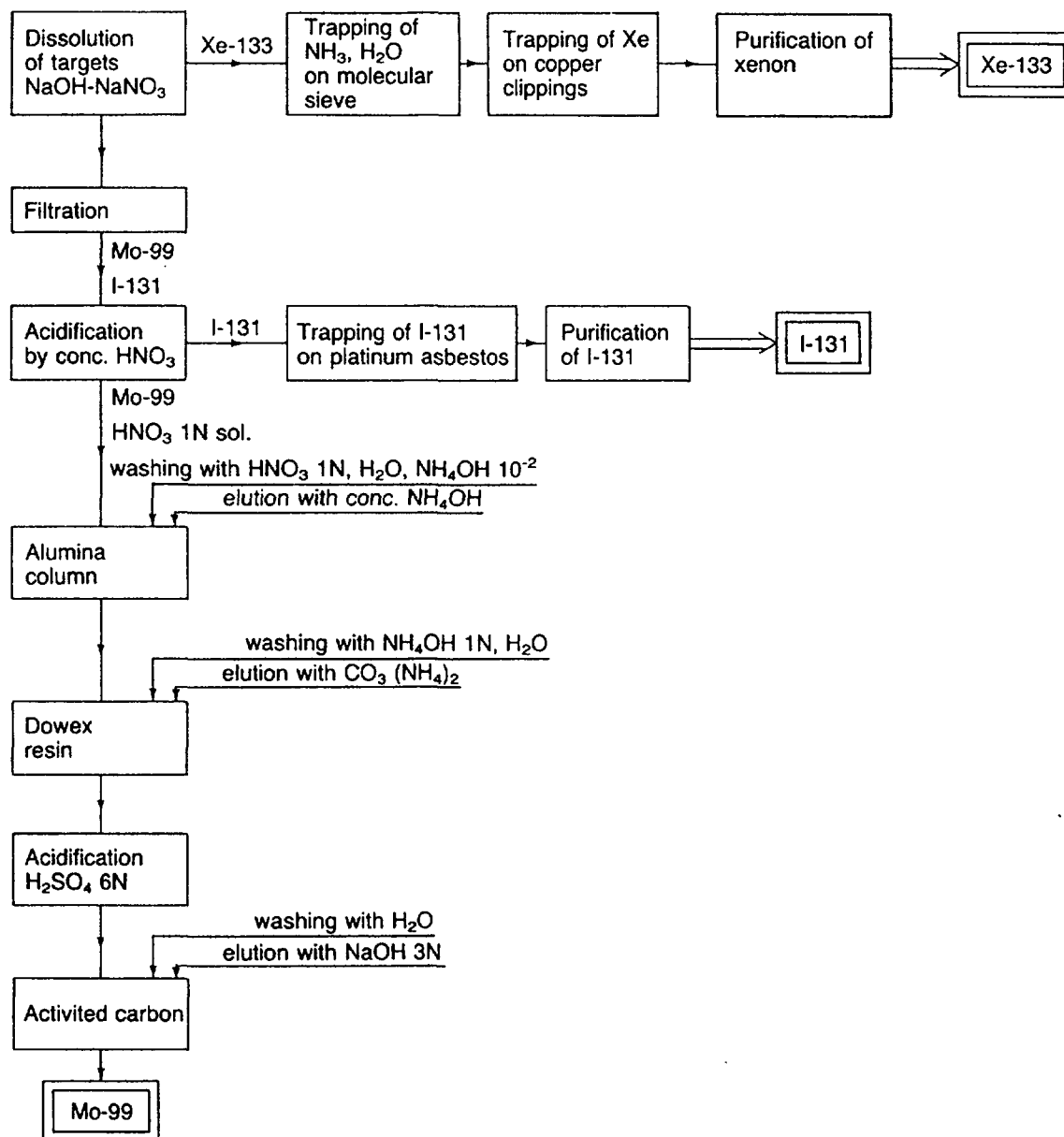


Fig. 1

4.2.4. Alumina column

The 1N HNO₃ acid solution is passed through an alumina column (WOELM A, SUPER 1). The Mo-99 is adsorbed on Al₂O₃ while 90 % of the fission products are eliminated to the waste in the fixation effluents and in the subsequent phases HNO₃ 1N, H₂O and NH₄OH 10⁻²N.

Mo-99 is then 90 % desorbed by concentrated NH₄OH. The column is submitted to further washing with H₂O and NaOH 3N in view of its regeneration and reutilization in the following cycles.

4.2.5. Dowex column and activated carbon column.

The Mo-99 of the NH₄OH (2.000 ml) eluate is fixed on 1 × 8 Dowex resin (200-400 Mesh) which is next washed with water, then eluted with CO₃(NH₄)₂ 1M (200 ml)).

The eluate is acidified with 6N sulphuric acid and passed through a column of activated carbon. After fixation, washing is done with H₂O and finally elution is carried out with 100 ml NaOH 0.3N. The Mo-99 yield of this operation is about 85 to 90 %. The final solution is sampled to measure volume activity and radionuclidic purity.

5. STUDY OF THE PROCESS

The operating of the process was examined successively at the tracer level in the laboratory, on the production installation at increasing production level and finally in the normal state of production.

Indicated below are some of the important characteristics of the observed process during the first two stages of the study.

5.1. Tracer tests

The goal of these experiments was to measure the yields of the different operations and to select the best working conditions.

The behaviour of Mo-99 and I-131 was given particular attention during acidification and chromatography on Al_2O_3 .

5.1.1. Operating conditions

Dissolutions were carried out on quantities of material corresponding to the weight of the 3 targets: 87.3 g Al and 18 g UAlx (12.9 g U).

The addition of the tracers was done in the dissolver, simultaneously with the adding of the carriers Mo (32 mg) and I (6.7 mg), in quantities corresponding to the expected weights of these elements at the time of dissolution.

5.1.2. Results

The tracer tests revealed the following elements :

- upon acidification : release of iodine : 80 to 90 %;
- on Al_2O_3 : fixation yield of Mo-99 : 99 %;
fixation yield of I-131 : 10 to 20 %;
elution yield of Mo-99 : 85 %;
- on Dowex : fixation yield of Mo-99 : 99 %;
elution yield of Mo-99 : 95 %;

The curves describing the behaviour of Mo-99 and I-131 on Al_2O_3 and Dowex are indicated in figures 2, 3 and 4.

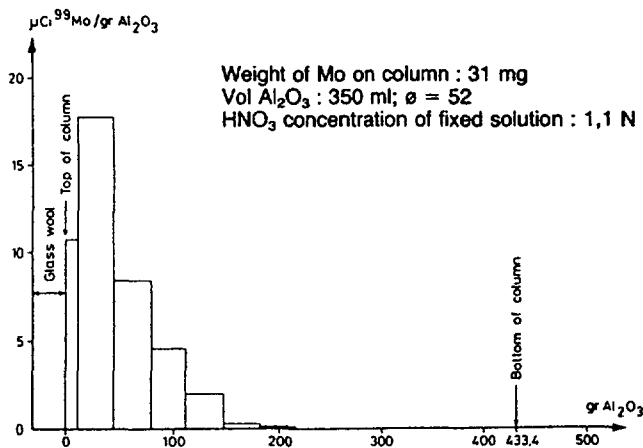


Fig. 2 : Adsorption curve of Mo on Al_2O_3

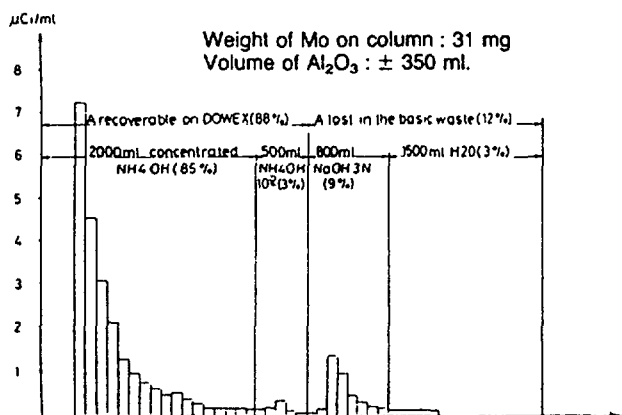


Fig. 3 : Distribution of Mo-99 : activities in the concentrated NH_4OH , $\text{NH}_4\text{OH } 10^{-2}$, $\text{NaOH } 3\text{M}$ and H_2O phases.

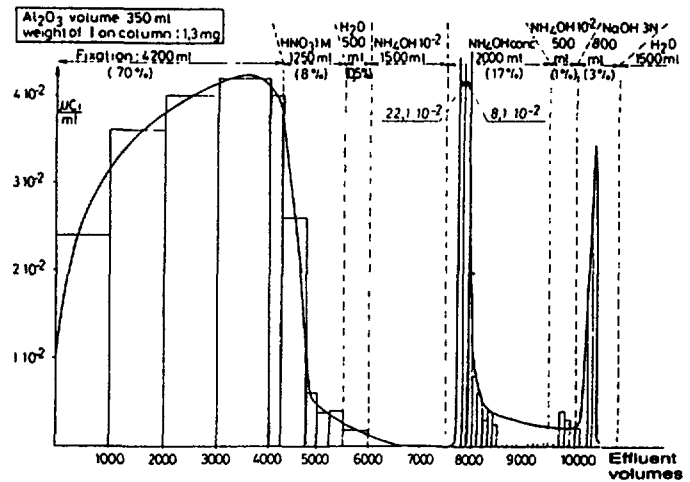


Fig. 4 : Distribution of ^{131}I volumic activities in the effluents of the alumina column

5.2. Tests at increasing production level

5.2.1. Operating conditions

Reprocessing was carried out seven times on irradiations having supplied activities of 1 to 50 Ci, 8dSR (8 days after removal of targets from flux). For the first four tests, final productions were 1 Ci, 2.4 Ci, 1.7 Ci and 22 Ci respectively.

In order to recreate the best expected chemical conditions at a high irradiation rate, carriers were introduced into the dissolver, prior to all operations.

All the experiments involved quantities of UAlx and Al corresponding to 3 targets. The quantities of carrier were :

- for the first 3 tests : 31 mg Mo
6.7 mg I
19.1 mg Cs
52 mg Ce
20.6 mg Ru
5.2 mg Sr

- for the 22 Ci test, these weights were reduced by 20 %.

Samples were taken during the entire process between acidification and the final solution and then controlled by means of Ge/Li spectrometry.

5.2.2. Results

The high number of observations recorded cannot be included within the context of this article. We will limit the presentation to a few important conclusions concerning the behaviour of the major contaminants of Mo-99.

The results were obtained on an installation almost in steady state. With an activity of a few curies, the possibility of carrying out a rigorous control on the results is excluded. That is why in regard to the columns, yields are expressed in relation to the sum of the activities contained in all the effluents. The hypothesis thus assumes that at the end of each production cycle, residual activities on Al_2O_3 are insignificant. The tests reveal that :

- on Al_2O_3 : — 99 % of caesium and cerium are eliminated in the acid and water fixation phases before elution;

- 95 % of ruthenium and tellurium are eliminated in the fixation and column acid washing phases,
- 50 to 90 % of the ruthenium remaining adsorbed on alumina comes off in the $\text{NH}_4\text{OH } 10^{-2}\text{N}$ washing effluents before elution,
- on the other hand, the tellurium remaining on Al_2O_3 is mainly desorbed in the basic waste by means of NaOH after elution;
- over 99 % of the Zr-95/Nb-95 and Ba-140/La-140 are found in the acid effluents;
- on DOWEX resin
 - the 2 major contaminants are Ru-103 and I-131,
 - above this column, rates of 96 to 99 % purity were measured,
 - the two subsequent phases of the process Dowex elution and chromatography on active carbon make it possible to meet the specification

6 ROUTINE PERFORMANCE

Total production yields are estimated for Mo-99 to be between 75 and 80 %. Depending on the reactor used, productions of 300 to 500 Ci post-calibrated 8 days after removal of the targets from the reactor (8dSR) can be realised on 6 target batches

Parallel to the Mo-99 production, productions of 125 Ci I-131 and 600 Ci Xe-133 (at 8dSR), can be obtained

The quality control results obtained for various successive batches are indicated in the following table for the 3 isotopes, on Monday at 12 noon, 8 days after removal, of the targets from the flux

Mo 99 $t_{1/2} = 65.93 \text{ h}^*$

Impurity	$\frac{\text{I 131}}{\text{Mo 99}}$	$\frac{\text{Ru-103}}{\text{Mo-99}}$	$\frac{\text{Zr 95}}{\text{Mo-99}}$	$\frac{\text{Sr 89} + \text{Sr-90}}{\text{Mo-99}}$	$\frac{\text{Total } \beta\gamma}{\text{Mo 99}}$	$\frac{\text{Total } \alpha}{\text{Mo 99}}$
Batch Nr	8 02 d	39 255 d	64 02 d	50 55 d 28 82 y		
Specification	$\leq 5 \times 10^{-5}$	$\leq 5 \times 10^{-5}$		Sr-89 $\leq 6 \times 10^{-7}$ Sr 90 $\leq 6 \times 10^{-8}$	$\leq 1 \times 10^{-4}$	$\leq 1 \times 10^{-5}$
4A16/03S	$\leq 2 \times 10^{-6}$	$\leq 1 \times 10^{-7}$	$\leq 2 \times 10^{-6}$	$\leq 4 \times 10^{-8}$	1.9×10^{-7}	$\leq 2 \times 10^{-11}$
4A18/04S	$\leq 2 \times 10^{-6}$	$\leq 3 \times 10^{-6}$	$\leq 2 \times 10^{-6}$	$\leq 4 \times 10^{-8}$	$\leq 1 \times 10^{-7}$	$\leq 2 \times 10^{-11}$
4A23/05S	$\leq 2 \times 10^{-6}$	3.8×10^{-7}	$\leq 2 \times 10^{-6}$	$\leq 4 \times 10^{-8}$	4.8×10^{-7}	$\leq 2 \times 10^{-11}$

I-131 $t_{1/2} = 8.021 \text{ d}^*$

Impurity	$\frac{\text{I 133}}{\text{I-131}}$
Batch Nr	20.9 h
3K14/21S	1.8×10^{-2}
3K28/21G	1.8×10^{-2}
3L12/22G	1.5×10^{-2}

Measured specific activity 80,000 Ci/g

The specification of radionuclidic purity amounts to 99.9 %. This will be complied with no later than four days after additional decay

7 CONCLUSION

The recovery of Mo-99 from irradiated fuel targets is complex and requires heavy investment. This technique also implies the utilization of enriched U-235, resulting in additional surveillance and management costs. It is, however, the only way to ensure batch productions of several hundred curies and to guarantee high specific activities necessary in the manufacturing of Tc-99m generators

In the method developed at the I R E, the same irradiation makes it possible to ensure production of Mo-99, I-131 and Xe-133. The economic significance of this formula is obvious. The technique used has made it necessary to develop effective trapping systems which enable greatly reducing the risks of having large quantities of I-131 and Xe-133 released in the ventilations

The procedure that has been described has been in operation since 1975 and supplies excellent results both from a quantitative and qualitative point of view. Rigorous organisation of irradiations and shipments guarantees operation regularity

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Xe-133 $t_{1/2} = 5.244 \text{ d}$

Impurity	$\frac{\text{Xe-131m}}{\text{Xe 133}}$	$\frac{\text{Xe-133m}}{\text{Xe-133}}$	$\frac{\text{Xe-135}}{\text{Xe-133}}$
Batch Nr	11.93 d	2.188 d	9.104 h
Specification	$\leq 3 \times 10^{-2}$	$\leq 3 \times 10^{-2}$	
3J10/19P	1.3×10^{-3}	1.0×10^{-2}	2.4×10^{-6}
3K07/21P	1.0×10^{-3}	1.5×10^{-2}	6.0×10^{-6}
3K21/20G	1.0×10^{-3}	8.5×10^{-3}	6.3×10^{-6}

* The half-lives are given for the contaminants. They are taken from an internal document, annually updated and published by the "Radioactive Measures" unit of I R E

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