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ANALYTICAL PROCESS CONTROL OF THE CELESTE R&D INSTALLATION OF IPEN-CNEN/SP

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Celeste-1 is a lab-scale hot cell intended for R&D work in reprocessing of low burn-up spent fuel elements. The studies are concerned with head-end, first separation cycle by Purex Process using mini mixer-settlers and development of analytical techniques. The analytical monitoring for process control purposes is based on several off-line techniques, such as X-ray fluorescence spectrometry, potentiometric titration, α- and γ-spectroscopy, spectrophotometry, fluorimetry, density measurement and gas chromatography. The analytical treatment takes place in a shielded working place analytical hot cell, glove boxes and hoods and some final measurements are made in the associated analytical laboratory. A pneumatic system is used for transporting analytical samples. All analytical procedures are ready and in operation.

INTRODUCTION

In a reprocessing facility, uranium and plutonium are separated from fission products and subsequently separated from each other by multi-stage counter-current

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extraction using tributyl phosphate diluted in n-paraffin as solvent. This is the world-wide known Purex Process[1]. Due to the intensive β-γ radiation of some fission products and high toxicity of plutonium and other α-emitters, the processing of spent fuel must be done in α-tight containement with biological shielding and remote handling equipment. In this type of installation, the process control is also difficult, requiring the development of some special working techniques and suitable equipment installations.

The task of process control is to provide information about the operation conditions of the plant. It is generally done by chemical analysis of sample solutions drawn from process streams[2,3]. On or in line analyses[4] are used in more sophisticated installations. The time taken for the analysis depends on the method used and the radiation level of the sample. Very high activity concentration level samples would normally require a completely remote-controlled operation. Small aliquot handling combined with appropriate sample preparation techniques are important aspects for selecting analytical methods. Under these conditions also previous chemical separation steps must possibly be avoided to reduce analytical waste.

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In this paper a description of analytical installations as well as analytical methods for process control are given.

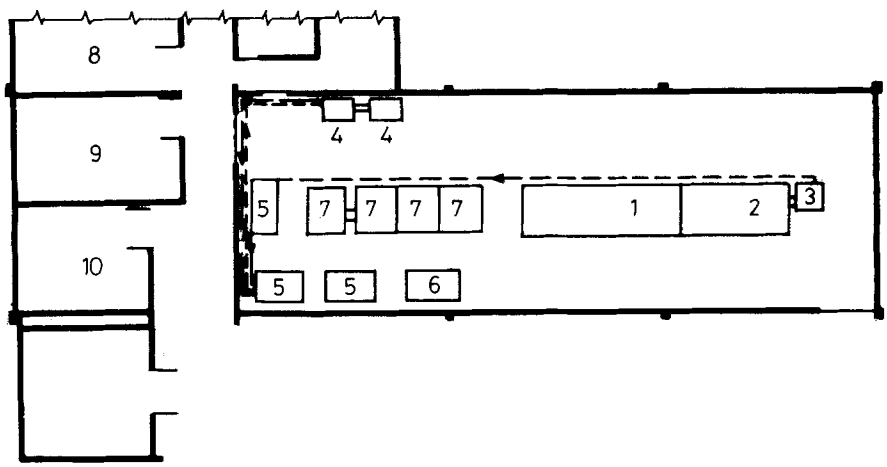

Fig. 1. Layout of Celeste.
1 - Process hot cell, 2 - analytical hot cell, 3 - intermediate glove box, 4 - analytical glove box, 5 - analytical hoods, 6 - process hood, 7 - process glove box, 8 - Lab-1, 9 - Lab-2, 10 - Lab-3

EXPERIMENTAL

Analytical instrumentation and installations

For chemical analysis, the following working places are available at Celeste: an analytical hot cell, two glove boxes arranged in line, three fume hoods for chemical treatment and three analytical laboratories as shown schematically in Fig. 1.

Analytical hot cell: shielded on all sides by 10 cm lead bricks, equipped with two master-slave manipulators. The following instruments are installed for chemical analysis or treatment of highly radioactive samples: remotely operated aliquotation device (ROAD), potentiometric titration device, extraction separation system, analytical flask opener system, sample storage rack, 4L capa-

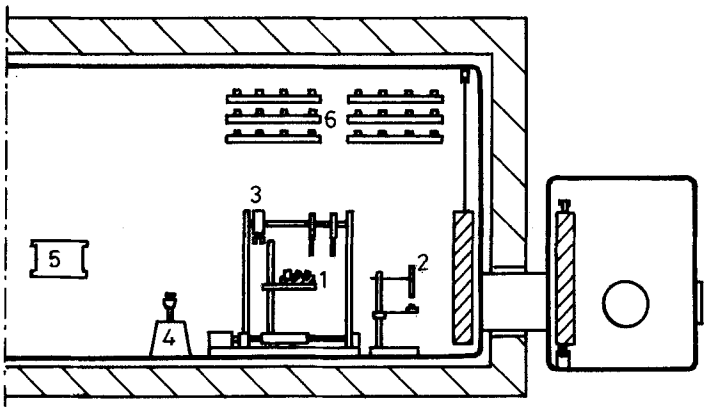

Fig. 2. Set-up scheme of analytical instruments in hot cell.
1 - Remotely operated aliquotation device,
2 - potentiometric titration device,
3 - analytical flash opener system,
4 - extraction separation system,
5 - analytical liquid waste storage tank,
6 - sample storage rack

city glass tank for liquid waste of analytical origin and polyethylene bottle for solid waste. The scheme of the set-up is shown in Fig. 2.

ROAD was manufactured by IPEN workshop and is composed of a stainless steel base plate for a small motor operated table (movable in the horizontal and vertical directions) and a rack where a pipette holder is fixed. In the remotely operated pipetting device, the pipette is connected to a small expansion vessel by a stainless steel capillary tube, which in turn is coupled with a micro-burette placed outside the cell. The burette, tubing and expansion vessel are filled with mercury. By the lifting movement of the burette piston, a desired volume of sample can be pipetted. Cross-contamination is avoided by the use of disposable plastic pipette tips. The schematic view of the ROAD is given in Fig. 3.

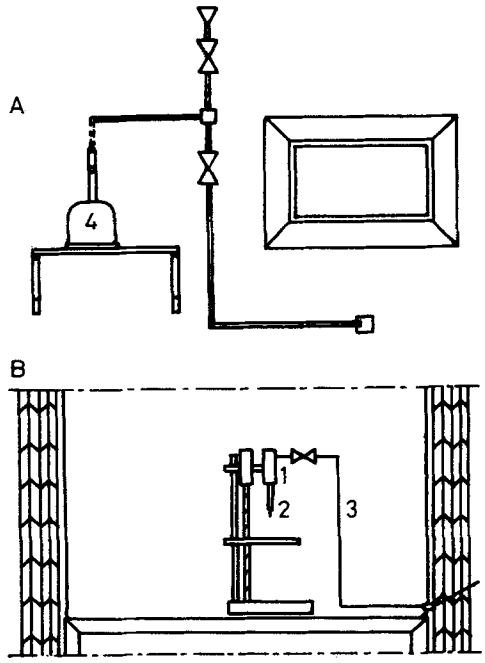

Fig. 3. Scheme of remotely operated aliquotation device. A - Outside of the cell, B - inside of the cell; 1 - Expansion vessel, 2 - disposable pipet tip, 3 - Hg filled capillary tube, 4 - microburette

Figure 4 shows the titration device with a mechanical stirrer and glass electrode interconnected by a plastic tube to the titroprocessor.

The analytical flask opener system is operated with a small motor to allow clock-wise and counter clock-wise movements and is fixed into a ROAD structure. The analytical cell is also provided with a storage rack for 100 sample flasks, which is fixed at the rear wall of the cell.

Glove box: two glove boxes are interconnected in series for analytical purposes. The first one for potentiometric titration, sample preparation for X-ray fluorescence analysis and the second one for photometric determina-

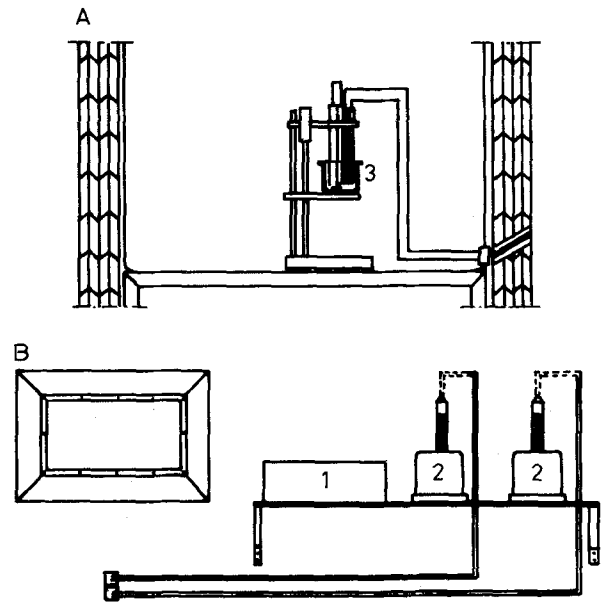

Fig. 4. Scheme of titration device.
A - Inside of the cell, B - outside of the cell;
1 - Titroprocessor, 2 - burette, 3 - titration unit with mechanical stirrer and glass electrode

tions. These boxes are equipped with a titroprocessor and optical fiber photometry (Fig. 5).

Fume hoods: three hoods are available for low level radioactive sample preparations. The first hood is used for Pu and Np chemical separations by TTA extraction and α-target preparation. Other analytical separations including the TBP degradation products are performed in the second hood. Finally, the third hood is reserved for fluorimetric analysis.

Analytical laboratories: there are three labs where more sophisticated equipment is installed for final measurements of analytical determinations. Lab-1 is assigned for X-ray fluorescence spectroscopy, Lab-2 for nuclear radiation detection and measurements (α- and γ-spectros-

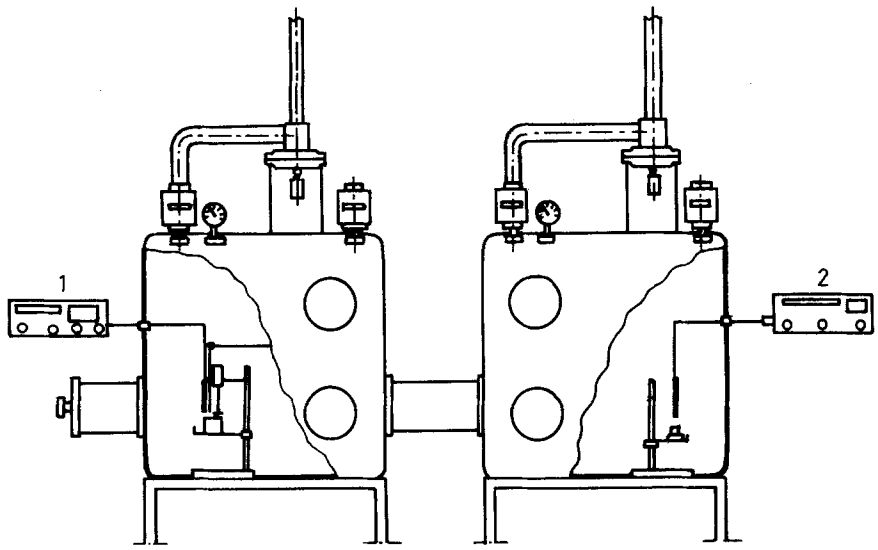

Fig. 5. Set-up scheme of analytical glove boxes.
1 - Titroprocessor, 2 - optical fiber photometry

copy) and Lab-3 for electrochemical instruments and gas chromatography.

Analytical sample transfer system

The pneumatic tube system for transporting analytical samples provides a connection between the hot cell and other working places. The analytical samples should always follow the general path: hot cell → hood → glove box → labs (see Fig. 1, dotted line).

Analytical methods

The analytical monitoring for process control purposes is based on several off-line measurements such as X-ray fluorescence analysis, potentiometric titration, α- and γ-spectrometry, fluorimetry and gas chromatography.

The most frequent analyses are these of uranium, plutonium, nitric acid, fission products, redox agents and TBP and its degradation products, in aqueous and organic phases.

The following analytical methods are ready and in operation:

Uranium

- X-ray fluorescence analysis using filter paper preparation[5].
- Photometric determination using DBM[6]. In some cases previous separation by hexon-TPAN extraction is necessary.
- Indirect potentiometric titration[7].
- Fluorimetric analysis is optional for very low concentrations. Prior separation by hexon-TPAN extraction is used.
- Optional density measurements for cold solutions[8].

Plutonium

- Alpha spectrometry[9]. Alpha targets are prepared by electroplating technique (calibration purpose) or evaporation technique (routine analysis).
- X-ray fluorescence analysis[10]. The intensity of the PuL_1 line is used as analytical line.
- Potentiometric titration[11].

Fission products

- Gamma spectrometry using Ge detector and γ-spectra analysis program[12,13].

Free acid

- Potentiometric titration[7].

Redox agents

- Nitrite: photometry using naphthylamine/sulfanilic acid reagent[14].
- Hydrazine: photometry using p-dimethylaminobenzaldehyde reagent[15].
- Uranium-IV: direct spectrophotometry[15].

TBP and degradation products

- Gas chromatography[16].
- Optional density measurement for fresh solvent[17].

DISCUSSION

In view of the maximum β-γ activity of 3.7×10^{11} Bq l^{-1} in Celeste, highly radioactive analytical samples are present only in the case of feed and HAW solutions. Such samples have to be remotely analyzed or chemically separated or diluted in the analytical hot cell. After the extraction cycle, the β-γ activity of process solutions is reduced and goes down in the course of the process. The analytical treatment of these solutions can be performed in non-shielded glove boxes under more favorable conditions.

In some cases, the final measurements are done in associated labs, as α-, and γ- and X-ray fluorescence analysis due to the difficulty of the box adaptation of the equipment which needs special constructions and materials. In these cases, cross contamination problems have been avoided by manufacturing safety sample transport devices.

All analytical methods were tested, first during the cold operations of Celeste and confirmed during the tests carried out with low activity irradiated uranium with good results.

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