PRESENTATION OF CEA MARCOULE LABORATORY DEPARTMENT

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ABSTRACT

The CEA Marcoule Laboratory Department initially dedicated to production support, has recently been renovated to perform a wide range of analyses to support dismantling of plant operation and process development units. It provides services to the operators of the CEA Marcoule Research Center in the fields of analytical chemistry, metallographic examinations, radioactivity measurements, in situ or online nuclear measurements, decontamination processes and industrial chemistry studies.
The facilities are designed to analyze all types of nuclear industrial and research samples both under inactive conditions and in glove box and hot cell environments. The Marcoule Laboratory today combines the skills of CEA researchers and AREVA NC analysts in support of production and R&D, process development and dismantling activities at Marcoule or other nuclear sites.

1. Historical Context

The Marcoule Laboratory Department was established in 1956 at the beginning of the site which was the birthplace of plutonium production in France. The laboratory was commissioned in 1958, in support of the Marcoule fuel reprocessing plant (Usine de Plutonium N°1 called UP1) and auxiliary units including the radioactive effluents treatment plant, the solid waste treatment plant.
Its routine activity involved two or three 8 hour shifts related to quality and process control. Three extensions were added to the initial facility building between 1960 and 1986 to meet to the new needs and expectations of the site.
The range of activities included the following:

- Online process control (chemical and radiological) via a pneumatic transfer network between plutonium production units and the Laboratory.
- Quality control on raw materials and finished products.

Since the shut down of UP1 in 1997, the Laboratory made some evolutions of its activities; they were shifted towards support dismantling activities (i.e.UNGG reactors), beginning with the removal of radioactive material and rinsing of the process loops. These activities require large numbers of samples with chemical preparation followed by chemical and physical characterizations. The analysis results obtained in this step are fundamental for further waste treatments to guarantee safe decommissioning operations and waste decategorization. The treatment and conditioning of small quantities of exotic radioactive wastes such as organic effluents or highly contaminated wastes also began at that time.
In addition to this huge analytical demand, the laboratory has been reconfigured at the same time in term of safety taking into account the new rules (i.e. fire and earthquake resistance) and in terms of capabilities to support research & development and dismantling.
This renovation will continue until 2010 with final approval by the safety authority in 2011. This paper describes the CEA Marcoule Laboratory Department.

2. Resources and Capacities

The Laboratory Department facilities are currently composed of 5 interconnected building wings covering a total ground area of about 4200 m^2 (fig. 1):
The Laboratory is divided into:

- Unrestricted access zones dedicated for non nuclear areas including the locker room, storage areas, yards and offices (1700 m^2).
- restricted access zone, the workplaces are distributed over 80 fume cupboards, 40 glove boxes and 35 shielded cells (2500 m^2).

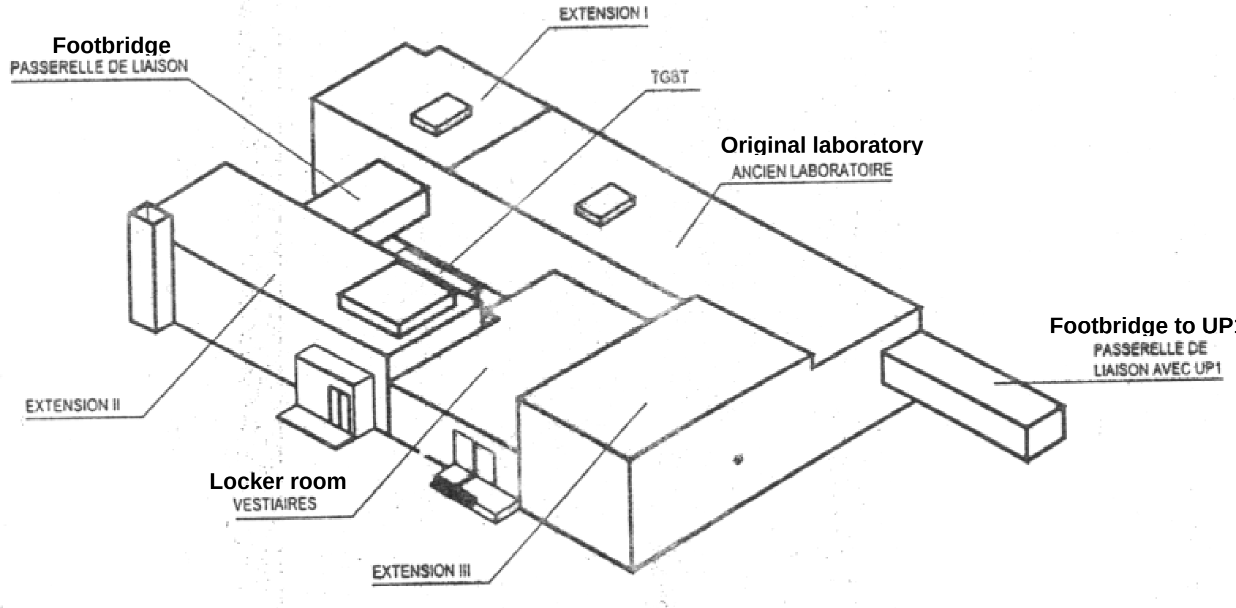

Fig. 1: schematic view of the Laboratory building

The Laboratory Department is operated by AREVA NC/Nuclear Site Value Development Business Unit under CEA/Nuclear Energy Division responsibility. It is staffed by 109 persons: 96 persons from AREVA NC (working 3X8 and 2X8 hour shifts) and 13 persons from the CEA.
Since 2008, 2 CEA teams have joined the Laboratory because AREVA NC and CEA intend to consolidate and reinforce the analytical and process competences of the Site in a same location in order to promote dynamic synergies between the teams. This cooperation could contribute to meeting the challenge and expectations in the future for Marcoule or other nuclear industrial plants and research centers.
The Laboratory Department is composed of:

- AREVA NC contribution

  - Central management entity (management, safety, security, quality, environment unit): 7 persons
  - General Service (Utilities, Radioprotection): 19 persons
  - Analytical Chemistry Laboratory: 31 persons
  - Nuclear Methods and Measurement Design Laboratory: 10 persons
  - Industrial Chemistry and Projects Laboratory: 15 persons
  - Radioactive Measurement Laboratory: 15 persons

- CEA contribution

  - Metallography and Chemical Analysis Laboratory: 10 persons
  - Advanced Decontamination Process Laboratory: 3 persons

The analytical and study capacities of the laboratory could be illustrated by the following data for 2008: treatment of 5000 samples processes by 23550 analytical determinations requiring 95000 working hours. About 1/3 of this time is dedicated to the studies (31600 working hours).

3. Missions

With the renovation and upgrade program, the Laboratory Department is able to perform a wide range of analyses to support dismantling, plant operation and process development activities, combining the skills of CEA researchers and AREVA NC analysts.
The Laboratory Department has an important technical and analytical means with competent personnel and is organized to respond to the following integrated production processes:

- Full Service laboratory function
  - Performance of analysis programs.
  - Multiple clients and diverse analytical activities: CENTRACO, MELOX, Phenix, EDF, etc…
  - Identification of complex samples (poorly controlled processes).
  - Task organization, response times, priority management.
  - Communication of results in various forms.
  - Complex approval of results (allowing for historical background).
  - Preparation of cost estimates, cost allocation and invoicing.

- Production quality control laboratory function
  - Regular sampling plans per unit, per sampling point, per campaign, etc.
  - Allowance for process operation (3X8-2X8 hour shifts, short response. time, real-time communication with various contacts).
  - Statistical control of the analytical process.

- Research and development laboratory function
  - Multiple client profiles (from research to industrial development).
  - Projects, studies and characterization development.
  - Possible interpretation of requests for services.
  - Analysis process not predefined and subject to dynamic modification.
  - Insufficiently documented tests.
  - Tracking and long-term interim storage of aliquot samples.
  - Complex consolidation of results.
  - Incorporation of results in reports.
  - Complicated scheduling.
  - International collaborations (Europe, US).

In technical and scientific fields, the laboratory department is active in analytical chemistry, metallographic examinations, radioactivity measurements, *in situ* or online nuclear measurements, decontamination processes and industrial chemistry studies to meet the following analysis requirements:

- Characterization of raw materials, nuclear waste and finished products.
- Process control in continuous operation.
- Testing and examination in support to R & D programs.
- Treatment and conditioning of small quantities of exotic waste with high alpha and/or beta contamination.
- Fabrication and supply of working standards and reference materials.
- *In situ* nuclear characterization.
- Characterization and expert examination.

Studies are carried out primarily in response to requests for:

- Assistance to plant operators concerning specific process-related problems.
- Pilot testing to adapt new or redesigned processes.
- Participation in programs of general interest.
- Treatment of liquid and solid waste rich in alpha and/or beta emitters.

- Decontamination of liquid effluents at prototype scale.

The Laboratory Department provides Studies and Analysis for many customers (mainly in the nuclear fields) including the CEA, AREVA NC, AREVA NP, MELOX, EDF, COMURHEX, and SOCODEI.
It is also involved in collaboration with numerous academics partners (Universities of Montpellier, Barcelona, Bordeaux, Limoges, Nancy, CNRS), Nuclear Research Centers (ITU, PSI, SCK/CEN, ORNL) and industrial partners (CANBERRA, THERMO ARL) to develop instrumentation devices and analytical operating procedures.
The expertise of the Department is well recognized by i) the presence of 3 senior experts (instrumentation and nuclear analyses), ii) 3 international experts ISO TC 85/WG5 and ENTRAP/WGA and iii) two AFNOR-BNEN national experts in nuclear waste fields who participates in various standardization working groups.
Finally, many analytical specialists belong to 8 working groups of the CETAMA, the CEA / AREVA organization devoted to the promotion of good practices and method validation in analyses for nuclear needs. By it ISO 9001 certification, the CETAMA (Commission d'ETAblissement des Methodes d'Analyses) allows to validate the quality of analytical methods by i) using prescripted methods developed by the members of working group, ii) using reference certified materials and iii) participating to inter-laboratory comparisons to test regularly the analytical capabilities of the teams.

4. Analytical and study Fields

The analytical and study activity is divided into 5 topics:

4.1. Analytical Chemistry :

This activity covers a wide range of capabilities in analytical chemistry in support of research, development and dismantling applications:

- elemental analysis of cations and toxic elements,
- specific analyses: CN^-, Cl^-, F^-,NO_2^-, NO_3^-, SO_4^{2-},PO_4^{3-}, $C_2O_4^{2-}$, formates, acetates, TBP, DBP, MBP, etc…
- Conventional chemical analysis: density, acidity, pH measurement, etc…
- Preparation and characterization: measurement standards, reactants.
- Pretreatment and preparation of samples before analysis: mineralization, dissolution (bitumen, concrete, etc.).
- Development of analytical procedures.
  - New XFR quantitative methods applied for multielement nuclear glass.
  - Characterization of the evolution of TBP under α irradiation.
- Waste and decontamination.

The analyses are performed by many devices in various environments:

- Monitored zone in conventional working conditions:
  - X-ray fluorescence (x 2).
  - ICP-AES (x 4).
  - ICP-MS (x 2) (fig.2).
  - C/S analyzer. Atomic absorption spectroscopy.
  - GC-MS and µ GC (x2).
  - Optical Asbestos identification.
  - Ignition point, flash point.
  - Liquid chromatography.
  - Ion chromatography.
  - FTIR.

Fig. 2: ICP-MS in conventional working environment

- Fume cupboard environments:
  - ICP-AES.
  - Liquid chromatography.
  - Atomic absorption spectroscopy.
  - UV-visible spectrometry.
  - Mineralization, dissolution.
  - TOC analyzer

- Glove box environments:
  - ICP-AES.
  - C/S analyzer.
  - UV-visible spectroscopy.
  - Particle size analysis.
  - Mineralization, dissolution (fig.3).
  - Liquid chromatography, GC-FID
  - XRD

Fig. 3: Mineralization in glove box

- Shielded line:
  - ICP-AES (fig.4).
  - Liquid chromatography.
  - UV-visible spectroscopy.
  - γ Spectrometry, specific electrodes, etc...
  - Mineralization.
  - Balance, microwave oven, density, etc…

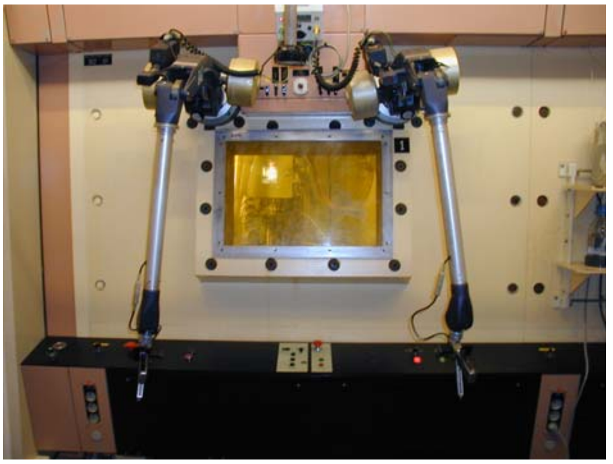

Fig. 4: Analytical hot cells (ICP-AES)

4.2. Metallographic Characterization

This activity provides expertise and characterization of materials at local scale (about one square micrometer) complementary with more global chemical analyses more global. It supports research, development and industrial studies and projects concerning Gen IV fuel and structural applications, front end:

- Quality control of materials, fuels (UO_2, USi, UMo, UCe) and components as received (bulk, deposit, powder): microstructure, adherence, homogeneity, welding.
- Examination of materials (steel, ceramic, glass, polymer, composite) after corrosion or aging tests: intergranular corrosion, reactivity mechanism by gas, liquid metal, molten salts or Uranium materials as UC, UN.
- Examination of industrial components: failure, corrosion by UF_6, Cl_2, CFC, HF.

The metallographic characterizations are performed by many devices in monitored zone in conventional working conditions:

- Metallographic preparation (cutting, polishing, etc…).
- Optical Microscopy: image and image analysis.
- SEM-FEG/EDS (fig.5) and SEM-low vacuum/EDS: image and local chemical analysis.
- Electron Microprobe (EPMA): quantitative chemical analysis.
- X-Ray Diffraction: phase identification.
- Macro-microhardness.

Fig. 5: SEM-FEG/EDS

4.3. Industrial Chemistry and Project

This activity is dedicated to the analytical development and control in support of industrial processes. It has a strong interaction with the analytical units in the Department.
The variety of the samples leads to work in 3 types of workstations:

- ventilated hoods for low contaminating samples
- glove boxes for contaminating and low irradiating samples
- shielded cells for the most active samples (fig. 6)

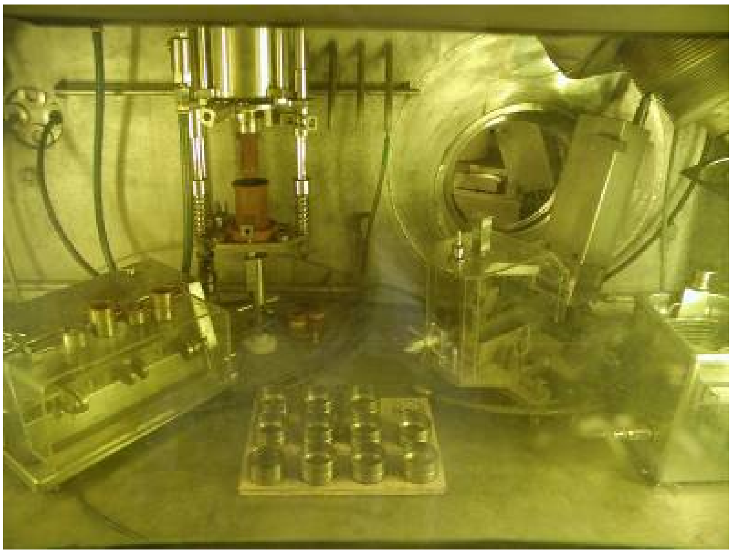

Fig. 6: sample preparation in hot cell environment

This activity is supported by its own analytical devices in various environments:

- Characterization of active samples:
  - Sampling : tools design and assistance to the operator
  - Macroscopic examination in shielded cells
  - Mechanical treatment (cutting, grinding, sieving…)
  - Chemical treatment (acidic dissolution, purification, separation…)
  - Specific analytical means (µcalorimetry, DTA/MS-DSC, GC)
  - Physical characterization (densities, water rate, graphite rate…)
  - Explanation and reporting of the results to the customer
- Back-up to Marcoules's nuclear facilities
  - Study and validation of new chemical processes
  - Recovery and recycling of Pu
  - Co-precipitation and reactivity tests for acceptability of big quantities of liquid effluents in Marcoule's Treatment Station
- Cement encapsulation
  - Validation of the formulation
  - Quantification of gas releases (GC)
- Destruction of active organic matter :
  - Supercritical water oxidation process (fig. 7)
  - Treatment of Pu-charged resins through silver (II)-electrodissolution and oxalic conversion.
- Specific work :
  - Dissolution of a irradiated UNGG fuel element
  - Qualification of a nuclearized analytical device (LIBS) for future *in situ* measurements
  - Decontamination of debased organic solvents

Fig. 7: supercritical set-up for separation processes

This activity also runs the laboratory of Marcoule's pilot facility and is in charge of the analytical support to the dismantling of this building. Many up-to-date analytical means are settled

- In glove boxes: X-ray fluorescence, LC, potentiometry, acid-base titration, overall α and γ counting, COD, foam testing, GC/FID…
- In shielded cells: collimated γ spectrometry, spectrophotometry, LC, density measurement…

4.4. Radioactive measurements

This activity is dedicated to isotopic analysis, quantification of alpha, beta and gamma emitters;

- Uranium-plutonium balance.
- Isotopic compositions: U, Pu, B and Li.
- Determination of beta emitters : ^{3}H, ^{14}C, ^{36}Cl, ^{55}Fe, ^{59}Ni, ^{63}Ni, ^{90}Sr, ^{94}Nb, ^{99}Tc, ^{129}I, ^{151}Sm.
- Fabrication isotopic standards.
- Development of specific measurements (e.g. ^{99}Tc in bitumen-encapsulated waste, ^{129}I by ICP-MS).

This activity is supported by its own analytical devices in various environments**:**

- 2 thermal ionization mass spectrometers.
- 2 liquid scintillators
- 6 gamma spectrometers including one with sample changer.
- 7 alpha spectrometers with grid chamber detectors.
- 16 alpha spectrometers with semiconductor detectors.
- 1 ICP MS in fume cupboard (fig. 8).

Fig. 8: ICP-MS in fume cupboard

4.5. Nuclear methods and conception design

This activity is dedicated to in situ radiological characterization of used equipment items (glove boxes, tanks, crushing machine, etc…), decontamination and dismantling monitoring of industrial set up and plants, waste packages. A specific methodology has been developed at Marcoule adapted to industrial expectations (more particularly in UP1) since 1998 [1]. This topic was developed because the conventional radiological approach was not appropriate to the characterization of industrial devices due to large dimensions and complex shapes. So, if "samples" couldn't be analysed in the laboratory, the laboratory has to find a solution to make measurements in situ on the site before dismantling.
This approach could be broken down as follows:

- In situ initial radiological survey of complex configurations (fig.9 and 10).
- Monitoring of dismantling operations
- Local characterization of the waste
- Modelling of the residual activity taking into account of the real geometry of the pieces to assess the dismantling strategy (fig. 11) in term of costs, schedule and waste specifications
- Estimation of the Pu mass distribution with a correct uncertainty (1g up to 100g of Pu)
- Characterization of historique waste not well characterized
- Assessment of waste package management.

Fig. 9: Gamma Camera and In Situ Spectrometer System (ISOCS) Gamma probe positioned in UP1 plant

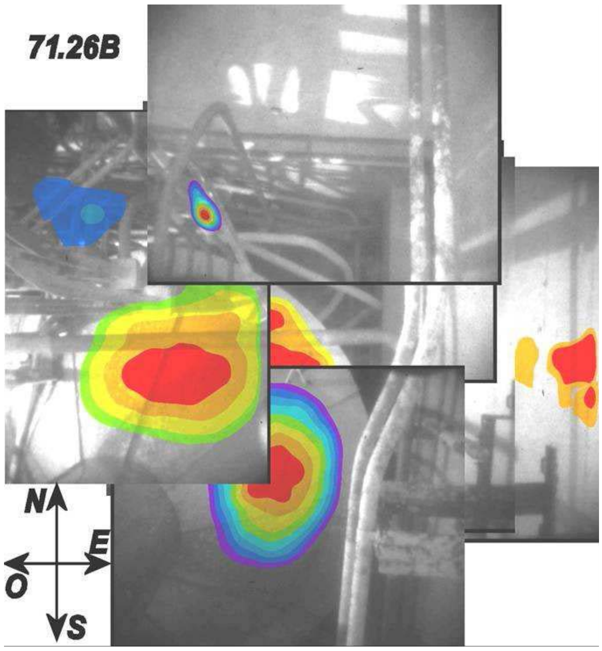

Fig. 10: Hot spots localisation in a used evaporator: superimposed images of visible-light image and gamma image.

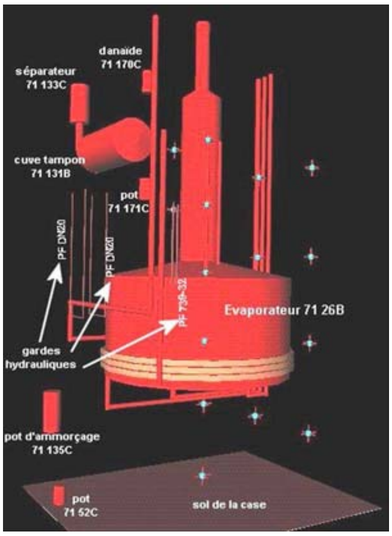

Fig. 11: modelling of the evaporator to evaluate the residual activity

The analyses are performed using portable devices and spectral simulation software:

- Gamma camera (CARTOGAM).
- Four portable Ge gamma spectrometry systems (coupled with ISOCS and PASCALYS software).
- Six portable Cd-Te gamma spectrometry systems (coupled with PASCALYS).
- NaI portable probe for fast hot spot survey
- Two dose rate measurement systems for pipes and other configurations.
- MERCURAD dose rate modelling software useful for dismantling scenario.

The specificity of this team is to group into a same entity most of the competences and know-how (radiologic and chemical measurements, modelling) needed to the monitoring of dismantling of industrial plant (about 100 equipments with Pu contamination treated at that time).

4.6. Example of the interest of the laboratory in the decommissioning and dismantling of UP1/Mar 200

A major program is in progress at Marcoule to dismantle the first French defence reprocessing complex UP1. This complex has been commissioned at the end of 50's and operated for

40 years. This extensive dismantling and waste recovery program must therefore cope with a large variety of waste and radiological situations. In many cases, operating events and poor documentation lead to a strong need of characterization activities prior to the studies or initiation of the dismantling operations. Those characterization programs are supported by the tools, analyses and expertise of the Marcoule Laboratory Department. Most of the collected data are used in the safety reports and the measurement methods, calibration and qualification techniques are part of the licensing process of each dismantling or recovery operation.

Example of the MAR200 dissolution unit:

One of the examples that best illustrates this program is the cleanup and dismantling of the continuous dissolvers located in Building 117 of the UP1 complex. The building contained two parallel dissolution lines (A and B).

For the line A dissolver, the initial analytical measurements revealed the lowest level of fissile material content in the deposits; these results allow to define the filtration parameters and to confirm the possibility of incorporating of the residues in the standard glass containment matrix. Based on these results and data, the safety report was approved. The recovery of the residues is now completed and the dismantling will start in 2010. All the residues have been completely vitrified.

For the line B equipment, preliminary inspection confirmed the existence of sludge and deposits at the bottom part of the dissolver. The in cell counters confirmed the presence of Pu and provided a rough estimate of the activity. A specific program to collect of 18 active samples was then defined and carried out.

Difficulties appeared in the sample collection as the sludge was located under the bottom support plate of the vessel. This perforated plate was about one inch thick and the preliminary rinsing test showed that the residues were partially blocked under the plate. In order to ensure fully representative sampling, the plate was removed by plasma cutting. The results obtained by the laboratory were taken into account on line for the definition of the interventions and the corresponding safety reports. The assessment of Pu content and its chemical and physical forms were of prime importance for defining of the sludge recovery technique. They were also considered in the safety report prepared for the future elimination route for the resulting waste. The analytical laboratory provided the project with more than 200 of physical, chemical and radiological data items under approved Q.A. conditions delivered in acceptable time. The required analyses included α, β, γ spectroscopy, chemical analysis of U and Pu, quantification of hydrogen in Pu, Pu isotopic composition, ^{90}Sr measurement, graphite quantification, chemical analysis of cations, anions, acetate, formiate as Pb, B, Ni, Cr total, Cr VI, As, Sb, Hg, Be, Se, Cd, CN.

The wide variety of available analytical techniques in the Marcoule laboratory was necessary to address the uncertainties on the sludge content, chemical composition and physical behavior under transfer and filtration conditions. Based on these results the recovery and filtration of the sludge is currently in progress.

Analytical techniques of the Marcoule Laboratory are also used for on line monitoring of D&D operations. In such cases, they mostly contribute to the waste characterization and elimination process. For example, such techniques have been successfully implemented for sorting metallic waste previously stored in pits. The low level counting equipment was installed on site and operated remotely. This allowed a direct and qualified characterization of the waste as LLW (low level waste), the waste were grouted on line without no additional handling or transfer.

5. Conclusions

This presentation has described the high technical potential and important analytical capacity of Marcoule Laboratory Department in the field of analyses, examinations and studies. It allows to treat analytical topics between laboratory to industrial scale. They were initially developed for Marcoule activities but these activities could now be proposed to other nuclear entities.

6. References

[1] S. Dogny, H. Toubon; Animma conference proceeding, Marseille (2009)