EXPERIENCE OF TRANSPORTATION OF RADIOACTIVE SAMPLES FOR ANALYSIS

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Abstract

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Independent verification of the concentration of special nuclear materials in the input solution, plant discards and product samples constitutes an important element of the state system of accounting or international safeguards for a reprocessing plant. This requires that the samples collected at the reprocessing plant are sent to the referee laboratory for verification analysis. Safe handling procedures and packaging codes have been evolved and are being kept constantly reviewed. During the reprocessing campaigns carried out at Prefre, India, under IAEA safeguards, a number of samples from stipulated stages of the process were sent to the Agency in discrete consignments. It was observed that verification analysis at the Agency's Analytical Laboratory involves considerable delay due to various procedural and logistic constraints in the transportation and co-ordination. This delay has certain implications for the verification system, the most notable being the problem of ageing of the samples. The paper describes experience in various aspects of transportation of samples, highlighting detrimental effects of ageing on the determination of elemental and isotopic composition in such samples. Corrective measures to be taken to compensate for these detrimental effects are also described in the paper.

1. INTRODUCTION

Reprocessing involves handling of special nuclear materials such as uranium and plutonium. Because of their extreme toxicity and also because of their strategic importance, the facility handling these materials maintains an accurate accounting system. In order to make the facility's material balance statement based on its measurements more credible, an independent verification of the plant's inventory is used. In the reprocessing campaigns involving IAEA safeguards, the independent verification is provided by the Agency's Laboratory. For this purpose, samples of the plant's input, discards and products are shipped to the safeguards Analytical Laboratory in Vienna. Air shipment is the commonly accepted mode of transportation of these samples. In spite of this, it is found that there are considerable delays

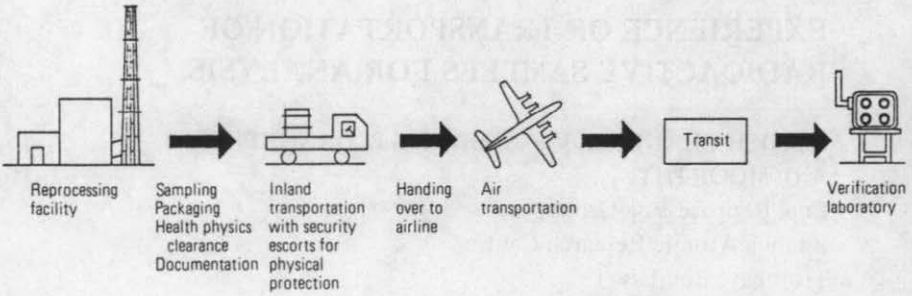

FIG. 1. Steps involved in the transportation of samples to verification laboratory.

in getting the samples analysed at the verification laboratory. These delays have two major implications:

(1) Because of the delay, a timely verification of the plant's inventory is not possible.
(2) Delays introduce uncertainties in the verification procedure due to the problem of ageing of the samples.

Various aspects of the transportation of radioactive samples to the IAEA with special emphasis on the problem of ageing of the samples due to delays in transportation are discussed in this paper.

2. SHIPMENT OF SAMPLES

During the reprocessing campaigns carried out at Prefre, India, under IAEA safeguards, a number of samples from stipulated stages of the process were sent to the Agency in discrete consignments. The steps involved in the shipment of these samples are shown in Fig. 1.

2.1. Sampling and aliquoting

Samples drawn from different key measurement points of the plant are aliquoted and given chemical treatment in shielded cells and glove boxes or fume-hoods. Details of the samples shipped are given in Table I. The input samples are diluted to nearly 150 times to bring down the associated fission product activity and hence the personnel exposure while handling the package. While the product samples are already in solid form, input and discard samples are also dried before being packed.

TABLE I. DETAILS OF SAMPLES SHIPPED FOR VERIFICATION ANALYSIS

No.	Inventory stratum	Nature of sample	Approximate amount of material in the vial	
			Uranium	Plutonium
1.	Input	Dried liquid	1.5 mg	5 μg
2.	Discard	Dried liquid	0.1 mg	1 μg
3.	Product (Pu)	Solid	300 μg	250 mg
4.	Product (U)	Solid	10 g	5 μg

Radiation level outside TNB-0145 container with about 60 samples: 1–5 mR/h (on contact).

2.2. Packaging

Suitable aliquots of samples are collected in glass vials which are loaded into the canisters. Each loaded canister is sealed in a PVC bag before being removed from the glove box to keep its external surface free of contamination. The canisters are packed into the container drums and sealed. Packaging is done in accordance with the codes and practices prescribed for each type of container. The sealed container is checked for loose contamination and radiation level before it is cleared for transportation. Packages come under yellow category II and transport index 0.5. Certified containers provided by the Agency, namely TNB 0145 and PAT-2 are used for transporting the samples. The TNB-0145 design conforms to the IAEA Safety Series No. 6, 1973 (revised 1979). The package is transported as Type B(U) fissile Class 1. This package can accommodate 50–60 vials in layers one over the other in fixed grooves in the inner container. The PAT-2 design meets all the requirements of NUREG-0360 under stringent accident modelling conditions and qualifies as fissile Class I package. Certification of both the containers for national regulatory requirements is carried out by the Division of Radiological Protection, Bhabha Atomic Research Centre.

2.3. Documentation

All relevant information pertaining to the shipment is carefully documented for reference by the facility and the Agency. Necessary freight documents such as the government clearance certificate, duty excise exemption certificate, dangerous goods certificates, etc., are also prepared.

2.4. Transportation

As the facility is located about 100 km away from the international airport, shipment involves transportation by road before the consignment is air freighted to Vienna. During inland transportation the consignment is provided with a security escort for the purposes of physical protection. The package is handed over to the airlines after the necessary shipment formalities have been completed.

3. DELAYS IN SHIPMENT

It has been observed that verification analysis at the Agency's Analytical Laboratory involves considerable delay due to various procedural and logistic constraints in the transportation. The factors contributing to the delay can be traced to three sources.

3.1. Pre-shipment delay at the facility

The economics of transportation dictate that a sufficient number of samples are collected for each consignment. This results in delays in sending the samples. Non-availability of transport containers at the proper time also contributes to the pre-shipment delays. Compared to these delays, the time taken for sampling, packaging and clearance is insignificant.

3.2. Transit delay

The major factors contributing to the delays in transit are procedural problems associated with: (a) awarding inland transport contract; (b) getting necessary clearances from various national and international authorities; (c) finding an air carrier cleared to accept the freight.

3.3. Post-arrival delay at the Agency

The long delay at the Agency is presumed to be due to the excessive work load of the verification laboratories and to problems in co-ordination with network laboratories.

3.4. Prefre experience

Results of a study conducted at random on three consignments sent from Prefre to the Agency are shown schematically in Fig. 2. It can be seen that on average it takes 40–50 weeks to get the results of verification analysis from the Agency. Of this, 18% of the delay is due to shipment problems and 52% is at the Agency end.

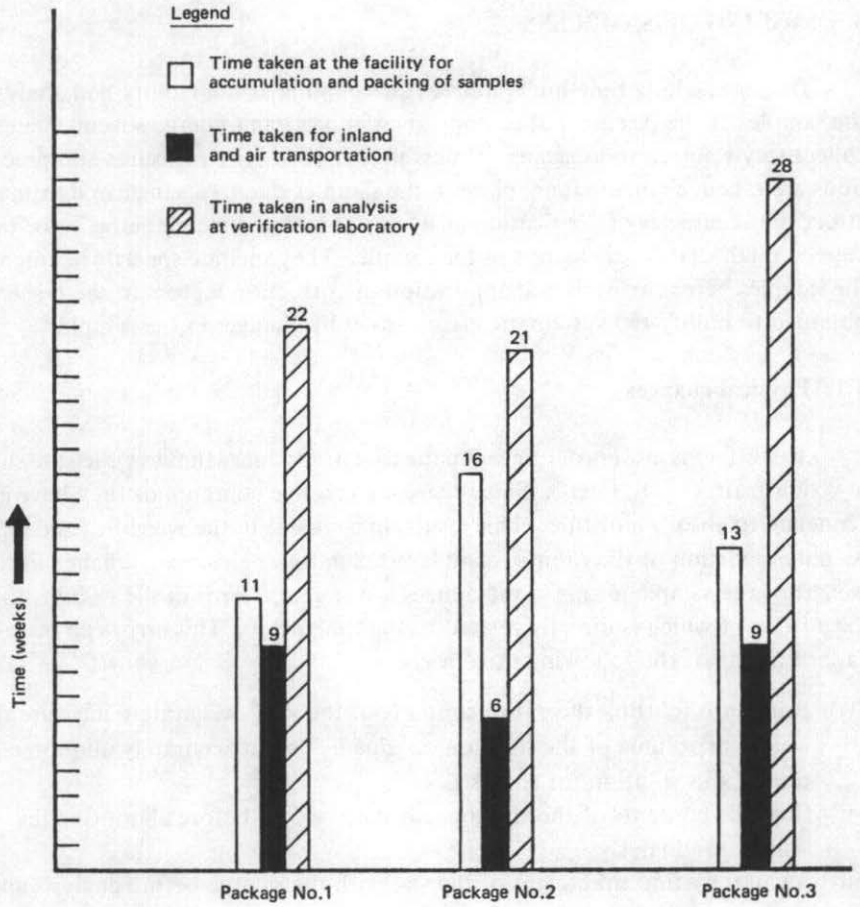

FIG. 2. Time study of sample packages.

3.5. Consequences of delays

The delay in getting the analysis results from the Agency has two major implications for the verification system. Firstly, the important objective of the verification system, namely, timeliness of detection of discrepancies in the inventory, is not met. The facility is forced to preserve a large number of archive samples till the reconciliation of results. This creates storage and radiation problems for the facility. Secondly, delays introduce uncertainties in the accuracy of the verification procedure due to sample ageing.

4. AGEING OF SAMPLES

During the long time interval between sampling at the facility and analysis of the samples at the Agency Laboratory, the samples can undergo several changes collectively referred to as ageing. Unless proper corrective measures and precautions are taken, changes taking place in the samples due to ageing can detrimentally affect the accuracies of verification analysis. The corrective measures to be taken depend on the nature of changes in the sample. They include special treatment to the samples before analysis and application of correction factors to the results obtained to nullify the systematic error caused by changes in the sample.

4.1. Physical changes

This effect is most pronounced in the case of product samples which are shipped in oxide form (U_3O_8, PuO_2). Since these are reactive compounds they have a tendency to absorb moisture. This results in a change in the weight of the sample. As only a portion of the shipped sample is taken for analysis, any change in the weight of the sample in transit introduces a systematic error in the results, the magnitude of which is directly related to the time delay. This error can be taken care of in one of the following three ways:

(i) Bring into solution the entire contents of the vial. Accurately measure the weight or volume of the solution obtained. Use an accurately aliquoted portion of this solution for analysis.

(ii) Heat the contents of the vial to a constant weight before aliquoting the sample for analysis.

(iii) Accurately find the weight of the vial with the sample before analysis and apply a correction factor to the result based on the change in weight of the sample. For example,

$$\text{Actual Pu content in a sample} = \text{Pu content at the time of analysis} \times \frac{\text{Wt. of sample at verification laboratory}}{\text{Wt. of sample at the facility.}}$$

4.2. Chemical changes

As a result of radiolysis, the chemical state of plutonium in liquid samples can undergo several changes. These include changes in the oxidation state of plutonium (from the Pu^{+4} state to Pu^{+3} or Pu^{+6} state) and changes in its chemical identity (from the ionic to hydrolysed or polymeric form). Traces of organic material present (in waste samples) can also complex the plutonium ions. These changes become more pronounced as time passes.

The mass spectrometry technique, which is the method normally applied for the accurate determination of plutonium in these samples, involves a vital step in

which the plutonium ion in the sample undergoes isotopic equilibration with a plutonium spike tracer added to the sample. Any change in the chemical composition of plutonium in the sample will adversely affect this isotopic equilibration and will lead to a bias in the measurement results.

Corrective measures for this effect include:

(i) Shipping the sample in dry form *after* mixing it with the spike tracer.
(ii) Repeatedly evaporating to dryness the mixture of sample and spike with concentrated nitric acid before shipment.
(iii) Treating the dry sample spike mixture with a mixture of nitric, perchloric and hydrofluoric acids before analysis at the verification laboratory. This treatment helps in restoring the chemical identity of plutonium in the sample by effectively depolymerizing or dehydrolysing or decomplexing it.

Some results of assay of a process sample, analysed immediately after and one month after sampling with and without such treatment (Table II) amply illustrate this point.

4.3. Radioactive decay

Radioactive elements undergo decay and in course of time change into entirely different species. Therefore, concentrations of these elements in a sample measured at different times significantly differ. The magnitude of the difference depends on the abundance of the particular isotope in the sample, its half-life and the time delay in measurements. The process solution sample in a reprocessing plant treating a PHWR fuel irradiated to about 6000 MW · d/t contain, among other isotopes of plutonium, significant amounts of ^{238}Pu and ^{241}Pu (0.1 and 3.85 wt.%, respectively); ^{238}Pu decays to ^{234}U by alpha emission and ^{241}Pu decays to ^{241}Am by beta emission. In view of their very short half-lives (87 and 14.1 years) the ^{238}Pu content of the sample decreases from its original value by 0.8% and that of ^{241}Pu by 5.2% within a short span of one year. Since the mass spectrometric determination of the total plutonium content of the sample is based on the accurate assay of the isotopic abundance, this decay will lead to a negative bias in the result. Change of ^{241}Pu content alone can lead to an error of −0.2% if the measurement is made after one year.

Hence, if the sample is analysed in the verification laboratory after a long time, a decay correction should be applied to the results:

Actual content of isotope A = Content of isotope A on the date of analysis

$$\times \frac{T}{2.t_{1/2}}$$

where T is the time delay in the analysis and $t_{1/2}$ is the half-life of isotope A (both in same units).

TABLE II. EFFECT OF AGEING OF PLUTONIUM SAMPLE ON ASSAY

No.	Assayed[a]	Conc. of Pu in sample (μg/g)		Random error in assay (%)		Relative deviation (%)[c]	
		Without treatment	With treatment[b]	Untreated sample	Treated sample	Untreated sample	Treated sample
1.	Immediately	4.335 (2)	4.353 (2)	0.14	0.82	–	–
2.	After 1 month	4.014 (14)	4.347 (1)	10.25	0.46	−7.79	−0.14

[a] With respect to sampling.

[b] Treatment with a mixture of $HClO_4$ + HNO_3 + HF.

[c] With respect to the value of a treated sample analysed immediately after sampling.

5. CONCLUSIONS

The present system of transportation of radioactive samples from the reprocessing facility to the analytical laboratory at the Agency's Headquarters involves considerable delay in the verification analysis. The delays introduce the problem of ageing of the samples which has a detrimental effect on the verification analysis. Though these effects can be compensated for by appropriate corrective measures the verification system is still extremely susceptible to inaccuracies. It is therefore necessary to review the entire transportation system with a view to substantially reducing the delays and making the verification procedure more meaningful.

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