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AUTHOR(S): K.K.S. Pillay

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Los Alamos National Laboratory
Los Alamos, New Mexico 87545

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TRACER TECHNIQUES IN ESTIMATING NUCLEAR MATERIALS HOLDUP

K. K. S. Pillay
Safeguards Systems Group, Los Alamos National Laboratory
P. O. Box 1663, MS E541, Los Alamos, NM 87545 (USA)

Residual inventory of nuclear materials remaining in processing facilities (holdup) is recognized as an insidious problem for safety of plant operations and safeguarding of special nuclear materials (SNM). This paper reports on an experimental study where a well-known method of radioanalytical chemistry, namely tracer technique, was successfully used to improve nondestructive measurements of holdup of nuclear materials in a variety of plant equipment. Such controlled measurements can improve the sensitivity of measurements of residual inventories of nuclear materials in process equipment by several orders of magnitude and the good quality data obtained lend themselves to developing mathematical models of holdup of SNM during stable plant operations.

Introduction

The potential diversion of special nuclear materials for possible clandestine uses is a serious problem facing contemporary society. Both national and international programs for safeguarding nuclear materials exist; still, the need to further enhance the capabilities of nuclear material safeguards is compelling. Current practices of nuclear material safeguards have three key elements, namely physical protection, materials control, and materials accounting. Although physical protection systems and materials control measures have important roles to play in safeguards, these measures by themselves cannot assure the presence of nuclear materials within a facility. The third element of safeguards, nuclear materials accounting, is an essential complement to other safeguards measures because it can keep track of nuclear materials within and across nuclear fuel cycle facilities.

Nuclear materials accounting consists of a series of activities carried out to establish the quantities of nuclear materials present within defined locations and the changes in those quantities within defined periods of time. Thus, accounting for fissile and fertile materials has become a necessary practice in all nuclear cycle facilities. Measurements of numerous physical and chemical forms of materials within processing plants are extremely challenging; the problems of estimating materials that remain as residuals in process equipment (holdup) are even more difficult. Large chemical processing facilities for nuclear materials contain hundreds of miles of pipes and ductwork, along with thousands of pieces of other equipment of various sizes and shapes, all capable of retaining small quantities of SNM per unit surface area adding up to large quantities of holdup. Locating and measuring these materials as part of materials accounting is a Herculean task, and the inevitable large uncertainty of holdup estimates often distorts the overall uncertainty of materials accounting for the whole facility.

One of the objectives of this investigation was to apply a well-known technique of radioanalytical chemistry, namely, tracer technique, to enhance the capabilities of nondestructive measurement techniques used in safeguards measurements. Using chemically compatible radioactive tracers, it was possible to improve the sensitivity of measuring residual inventories of uranium in processing equipment at least by two orders of magnitude. The results of such measurements were used to develop mathematical models of residue retention of nuclear materials in process equipment.

Holdup of SNM

The term "holdup" refers to residual amounts of SNM remaining in a process facility after the run out of bulk material. Identification and quantitative estimation of holdup of ^{235}U and Pu are often attempted

using nondestructive gamma-ray detection techniques.[1] Some of the inherent limitations of passive assay techniques for the measurement of residual amounts of enriched uranium and plutonium are

- the long half-lives (and consequently low specific activity) of the isotopes of ^{235}U and ^{239}Pu,
- the insensitivity of passive neutron assay techniques for the measurements of residual amounts of U and Pu, and
- the attenuation of gamma-radiations within the SNM and by the materials of construction of processing equipment.

In recognition of these limitations, the US Nuclear Regulatory Commission (NRC) has issued guidelines describing acceptable procedures for nuclear materials measurements in process facilities,[2-4] including the acceptability of other methods[2] such as "tracer or step function inventory" for nuclear materials measurements. Although the potential value of tracer techniques for SNM measurements has been suggested in the literature,[5-7] there have been no reports of any plant-scale applications of this technique for nuclear materials accounting.

Experimental studies using tracers

Tracers are powerful tools in the study of process kinetics, and they have been used extensively in the investigation of biological, geological, environmental, and chemical systems. Tracer techniques have been used in nuclear materials processing facilities for the measurement of flow, volume, and process kinetics.[8,9] An important aspect of a recent study[10] completed at the Los Alamos National Laboratory was an attempt to develop estimation models for materials holdup at SNM processing facilities. An integral part of this project was to conduct specially designed experiments to simulate industrial processes for nuclear materials production

and fabrication, and to collect data for developing holdup estimators that are equipment- and process-specific.

Details of holdup experiments

Three of the experiments where radioactive tracers were used to enhance the capabilities of nondestructive assay (NDA) of holdup were

(1) a uranium dust-generating operation at a highly enriched uranium processing facility,

(2) an ammonium diuranate precipitation and calcination process, and

(3) a solution loop system circulating uranyl solutions.

The first experiment involved the study of uranium holdup during a dust-generating operation in which two types of uranium oxide powder and one type of incinerator ash containing uranium were used. The experimental facility consisted of a glove box, some ductwork, and an exhaust air filter system. The total throughput of uranium through this experimental facility was approximately 1 kg/cycle for a total of 70 kg for seven experiments. The uranium used in the dust-generation experiment was intimately mixed with a neutron activated sample of the same material allowed to decay for 2 weeks. After each experiment (consisting of 10 cycles of dust generation), the residual amounts of uranium remaining in each piece of equipment were nondestructively measured using a specially mounted NaI(Tl) scintillation detector. The prominent gamma radiations of ^{95}Zr-Nb from the tracer were used to determine the amount of uranium present. This approach was used to measure the holdup of uranium in the glove box, in various regions of ductwork, and on the exhaust air filter system.

The second experiment consisted of the precipitation of uranium as ammonium diuranate (ADU) from uranyl nitrate solution, filtering out the ADU, and calcining it into U_3O_8. The precipitation processes were carried out in a large, cylindrical, stainless steel vessel. The filtered

ADU was calcined in Inconel-600 trays in a Lindburg furnace. The throughput of uranium through this system was about 1 kg/batch with a cumulative throughput of about 50 kg. A radioactive isotope of scandium (^{46}Sc) was used to follow uranium during all stages of this experiment and to measure the holdup of uranium in various pieces of equipment used.

The third experiment consisted of circulating two types of uranyl solutions in two separate loops, one built of stainless steel and the other fabricated from chlorinated polyvinyl chloride (CPVC). The loops were built to incorporate two large storage tanks, circulation pump(s), pipes of various dimensions, elbows, tees, unions, flow meters, valves, and pressure relief valves. One of the solutions pumped through the stainless steel side of the loop was a uranyl nitrate solution containing excess nitric acid (4 moles of acid per mole of uranium); the other solution, circulated through the CPVC side of the loop, was a uranyl fluoride solution containing excess hydrofluoric acid. The total throughput through the system was the equivalent of about 110 tonnes of uranium at a circulation rate of approximately 50-100 kg/h of uranium. Scandium-46 as Sc^{3+} and $[ScF_6]^{3-}$ were respectively used as tracers in each of these loops.

The objectives of the above mentioned controlled experiments included periodic measurements of the residual uranium in the system and attempts to correlate the throughput with holdup. In the early stages of designing these experiments, it was realized that it would be impractical to make the necessary measurements for these experiments by attempting NDAs of ^{235}U using scintillation gamma techniques. The quantities of materials to be measured during the experiments ranged from a few tenths of a gram to several grams of uranium in a variety of process equipment. The changes in the quantities of holdup of uranium between measurements were even smaller, and the difficulties of nondestructively measuring such small amounts of material in experimental facilities located in nuclear material processing plants were not trivial.

Production and use of tracers

In experiment (1), a neutron activated sample of (a) powdered uranium oxide and (b) an incinerator ash containing about 10 wt% of uranium oxide were used as tracers. These samples were irradiated in a research reactor until about 10^{15} fissions were introduced in the tracer sample. The irradiated samples were allowed to cool for about 2 weeks to reduce the level of short-lived fission products and to maximize the level of ^{95}Zr-Nb.

In experiments (2) and (3), a chemical analogue of uranium, namely, scandium, with a unique neutron activation product was used as the tracer. Scandium-46 isotope was produced by neutron activation of natural scandium in the form of Sc_2O_3. The properties of these radionuclides relevant to the tracer applications discussed here are summarized in Table 1.

Physical and chemical compatibility of the tracer with the uranium system is essential to the successful function of the additive as a true tracer for uranium. Carefully designed bench-scale experiments were performed to confirm that the tracers chosen followed uranium quantitatively throughout the process. Table 2 lists general features of the controlled experiments, and the compatible forms of the tracers that were prepared and incorporated into these experimental systems.

Results and discussion

Homogenization of tracers in uranium matrices

The incorporation of a tracer in a homogeneous solution of uranium is much easier than the introduction of tracer in a solid matrix as with the uranium dust-generation experiment. In this latter case, about 200 mg of U_3O_8 (or ash containing U_3O_8) were irradiated in a neutron flux to generate fission products within the matrix of U_3O_8. The active U_3O_8 (or ash) was then blended with the bulk material. The mixture was sampled and counted

to assure homogeneity of the tracer within the uranium oxide matrix. The blended material was considered homogeneous if the relative standard deviation of the specific activity of the samples was less than 5%.

The uranyl nitrate and uranyl fluoride solutions used different ionic forms of scandium because of the chemical characteristics of the media. Homogeneous mixtures of uranyl solutions and corresponding tracer forms were prepared and preserved, for up to 2 months, in containers made of the same material used in the experiment. The mixtures were periodically analyzed to determine the potential segregation of tracers from the uranium matrix. It was determined that the uranyl nitrate solution with Sc^{3+} was compatible with polyethylene and stainless steel loop and the $[ScF_6]^{3-}$ ion in uranyl fluoride was compatible with polyethylene and the CPVC loop with a hastelloy pump.

In case of the ADU precipitation and calcination, the uranium went from a homogeneous solution to a precipitate and then to a calcined solid. The tracer scandium also followed the physical changes with concomitant chemical changes. The basic chemical reactions of uranium and scandium during this experiment were as follows:

$$UO_2(NO_3)_2 + NH_4OH \rightarrow \text{precipitation} \rightarrow (NH4)_2U_2O_7.xH_2O$$

$$(NH4)_2U_2O_7 \rightarrow \text{calcination} \rightarrow U_3O_8$$

$$U_3O_8 + HNO_3 \rightarrow \text{dissolution} \rightarrow UO_2(NO_3)_2 \quad ; \text{ and}$$

$$Sc(NO_3)_3 + NH_4OH \rightarrow \text{precipitation} \rightarrow Sc(OH)_3$$

$$Sc(OH)_3 \rightarrow \text{calcination} \rightarrow Sc_2O_3$$

$$Sc_2O_3 + HNO_3 \rightarrow \text{dissolution} \rightarrow Sc(NO_3)_3.$$

Careful measurements of the movements of ^{46}Sc tracer with uranium showed no partitioning between uranium and scandium during dissolution, precipitation, and calcination processes, nor during recycling of the products in

the same process. These measurements indicated that scandium, a chemical analogue of uranium, is an excellent tracer for uranium during the transformations involved in this unit process.

Limitations of experimental facilities

The holdup experiments were conducted at two SNM processing facilities with large inventories of uranium and/or thorium. Figures 1 and 2 illustrate the nature of the interferences by the background radiations at the two facilities. Figure 1 shows the gamma spectrum of ^{232}Th and its daughters, which are the dominant background at the facility where the dust-generation experiment was conducted. In this illustration, the gamma spectrum of ^{235}U was inserted to show the relative location of the most abundant primary gamma peak from enriched uranium. Also included in this illustration is the gamma spectrum of a ^{95}Zr-Nb equilibrium mixture, which was the dominant activity of the tracer used. The gamma radiations from the tracer are clearly distinguishable and measurable in the midst of large background radiations from thorium and its decay products. Similarly, Figure 2 shows the background radiations at the uranium processing facility where experiments (2) and (3) were conducted using ^{46}Sc as the radioactive tracer. Here again, the advantage of using ^{46}Sc as a tracer for the NDA of uranium is obvious.

NDAs and cleanout measurements

The amount of radioactivity of the tracers used in these experiments ranged from 1 to 3 x 10^9 Bq/kg of uranium. For ^{46}Sc, this amounted to an atom ratio of approximately 1 tracer atom to 10^9 atoms of uranium.

The instrumentation used in these measurements consisted of specially designed and built shielded NaI(Tl) scintillation detectors and single-channel analyzers and scalers. With this simple instrumentation, it was

possible to quantify accurately the tracer levels (and, indirectly, the uranium residues) in a variety of complex process equipment.

A number of cleanout operations were performed followed by chemical and radiochemical measurements to compare the results of NDAs using radioactive tracers. The cleanout measurements were performed by a variety of methods for the various experiments reported here. Among the analytical techniques used were isotope dilution mass spectrometry, titrimetry, spectrophotometric analysis using Arsenazo-III, and gamma-ray spectrometric measurements of the tracer activity in cleanout materials using a well-shielded, high-efficiency NaI(Tl) detector coupled to a multichannel analyzer. In Table 3, the results of these cleanout measurements are compared with the corresponding values of NDA measurements of tracers in the residual holdup.

Calibration standards for NDA

Developing suitable calibration standards for NDA of radioactive nuclides is always a challenge. However, in the case of holdup measurements, the problems become extremely complex, due to the nonhomogeneity of the sample to be assayed, its unknown distribution pattern, varying chemical composition, the complex geometry of the equipment in which the materials reside, the attenuation of radiations by the equipment and the matrix, and the high background radiation levels in processing areas. Ideally, it is desirable to have calibration sources closely simulating the actual holdup deposits to be assayed. During this investigation a variety of standards were developed and used in addition to point sources, line sources, and flat area sources. Some of the unique designs of standards developed during this investigation include:

(1) Flexible plastic capillary tubes containing known weights of standard solutions of $^{46}Sc^{3+}$, which were shaped to fit the interior surfaces of precipitators, calciners, pipes, and pipe fittings.

(2) HEPA filters on which PuO_2 was uniformly distributed to simulate exhaust air filters containing PuO_2.

(3) A pump taken out of service containing residual deposits of uranium (and the tracer) was used as a calibration standard for similar pumps used later in the experiment. The amount of material in the (calibration standard) pump was later determined after carefully dissolving out the residues and determining the uranium content of the solution by spectrophotometric analysis. This concept of using identical pieces of equipment taken out of service was successfully extended to ductwork, pipes, and a variety of pipe fittings. Similar unique design and use of calibration standards for holdup measurements have been recently reported.[11]

Modeling of holdup

The accumulation of holdup, like many other physical processes, is amenable to modeling. When a processing facility operation is stable, holdup behaves as a smooth function of time, perhaps gradually increasing or nominally remaining constant. This aspect of temporal continuity in holdup behavior can be captured through modeling. A spacial continuity also may exist in the behavior of holdup. A proper combination of all such relevant information formalized through the use of a model leads to much improved holdup estimation compared to a single measurement value.

The use of models to obtain holdup estimates has been discussed in the literature[10,12] and is not elaborated here. An example presented below illustrates both the advantages and limitations of modeling to estimate

holdup. Data obtained from air filters used in the dust-generation experiment is a good example of increasing holdup with time. Figure 3 summarizes the results of three filters from uranium dust-generation experiments conducted under three different air flow rates in a glove box. In all these cases, holdup accumulation on filters is well represented by the model

$$H(t) = \alpha t + \beta t^2 \quad ,$$

where H(t) is the amount of holdup on the filter when the throughput is t kg, and α and β are constants. This illustration clearly shows the dependence of the constants α and β on specific operating conditions involved and demonstrates that the model developed for one set of conditions may not apply under another. Several potential advantages of holdup modeling are evident here. One is the benefit of retrospective estimation, that is, looking back in time to estimate holdup when a measurement was not done. A more important benefit is prospective holdup estimates or predicting future holdup.

Conclusions

The results of these experimental studies clearly demonstrate that the sensitivity of holdup measurements can be significantly improved (over two orders of magnitude) by the judicious incorporation of trace levels of radioactive nuclides of high-specific activity and desirable gamma-emission characteristics. This approach is particularly valuable in generating data for the development of holdup estimators and in determining significant holdup patterns of large processing facilities of strategically important nuclear materials. The cleanout measurements of materials holdup necessarily involve major disruptions in the operations of the facilities

and considerable investment of manpower and resources. The NDA measurements described here using tracers can be performed in a few minutes without disruptions of facility operations. Figures 1 and 2 clearly demonstrate that the passive assay of gamma radiations from the ^{235}U for the study of holdup in these experiments would have been futile because of the extremely low-specific activity of ^{235}U and the overwhelming interferences by the background radiations resulting from the large inventories of uranium and/or thorium. It is essential to have specially designed radiation detectors and calibration standards to minimize the uncertainties of the NDA measurements of nuclear materials holdup in process equipment.

The results of tracer studies described here were used to develop mathematical models of holdup in a variety of equipment under different operating conditions.[10] If it was not for the tracers, it would not have been possible to develop the good quality data that allowed us to develop models that represent the behavior of residual material accumulation in a variety of process vessels and equipment.

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Table 1

Specific activities of ^{235}U and tracer isotopes

Nuclide	Half-life	Prominent gammas (keV)	Gamma emissions (s-1.g-1)
^{235}U	7.04×10^{8} yr	185.7	4.32×10^{4}
^{46}Sc	83.85 days	889.3 1120.5	2.5×10^{15}
^{95}Zr-Nb	64.4 days (31.15 days)	724.2 756.7 765.8	1.56×10^{15}

Table 2

Radioactive tracers used in holdup studies

Experiment	Tracer	Holdup measured in
U-dust generation	^{95}Zr-Nb (in U_3O_8)	Glove box, ducts, tees, elbows, filters
ADU-precipitation & calcination	^{46}Sc as Sc^{3+}	Dissolver, filters, precipitator, calciner, calciner trays
U-solution loop	^{46}Sc as $[ScF_6]^{3-}$	Pumps, pipes, elbows, tees, unions, valves

Table 3

Comparison of NDA measurements of holdup with cleanout measurements (in grams of uranium)

Experiment no.	Equipment/ parts	Tracer NDA measurement	Cleanout measurement
1	Ductwork (fine U_3O_8)	3.56 6.22	3.59 5.10
1	Ductwork (ash with U_3O_8)	1.66 2.50	1.06 2.51
1	Ductwork (coarse U_3O_8)	1.60	1.89
2	ADU precipicipitation vessel	12.6 9.3	14.6 10.2
2	Calcining furnace	1.7	1.5
2	Calcining trays	1.4	1.3
3	Pipes (per meter)	0.37 0.16	0.40 0.15
3	Elbows	0.02 0.03	0.03 0.03
3	Valves	0.40	0.37
3	Tees	0.08 0.08	0.07 0.08
3	Pumps	13.7 9.4	11.9 7.0

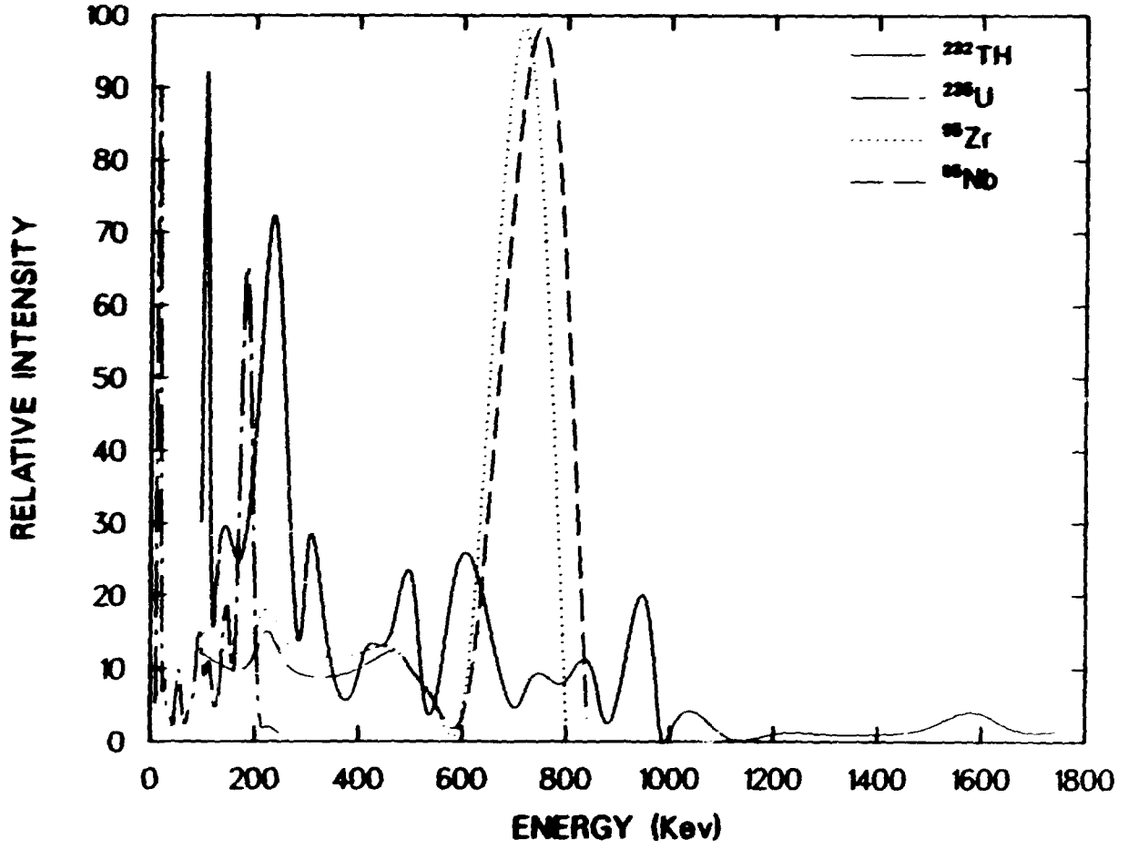

Fig. 1. A combination of the gamma-spectra of ^{232}Th and its daughters, ^{235}U, and the tracer nuclide ^{95}Zr-Nb.

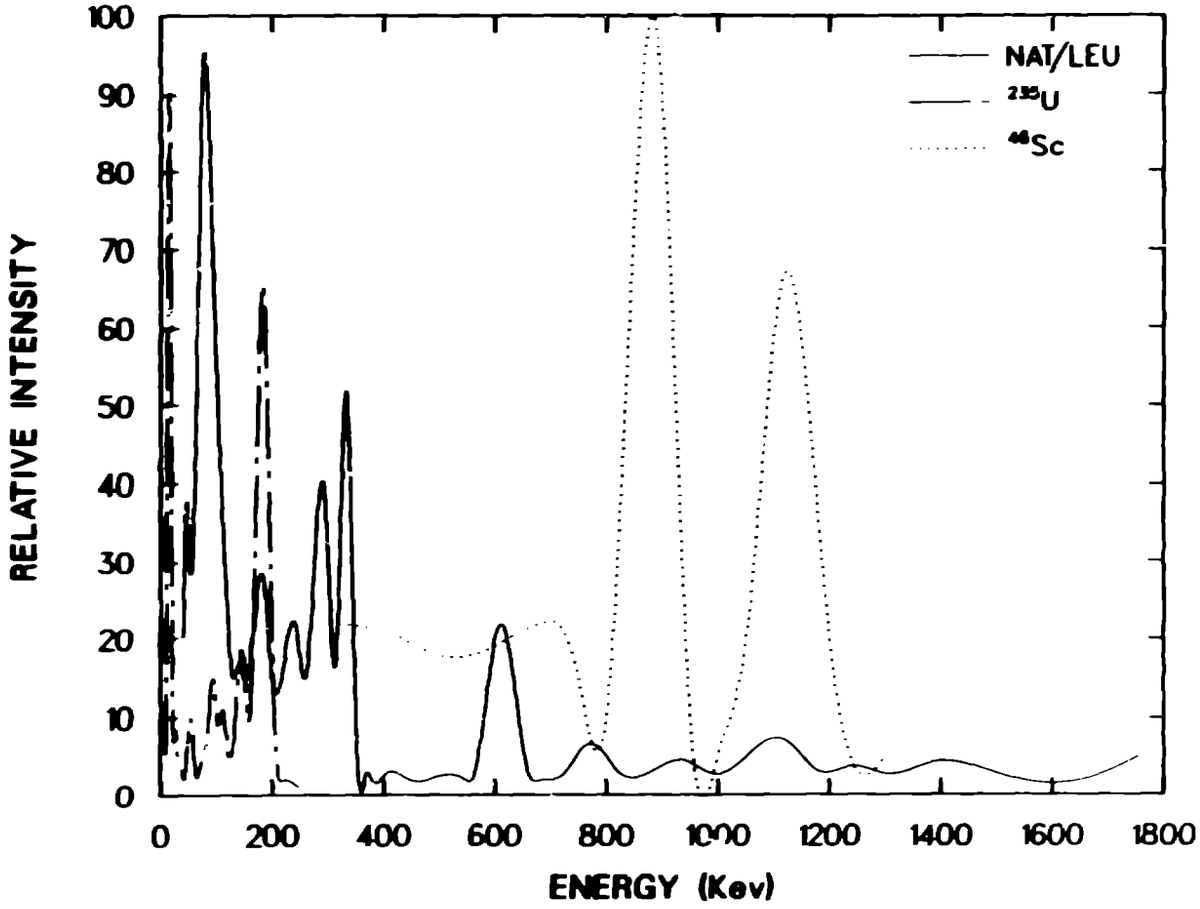

Fig. 2. A combination of the gamma-spectra of natural and/or low-enriched uranium, ^{235}U, and tracer nuclide ^{46}Sc.

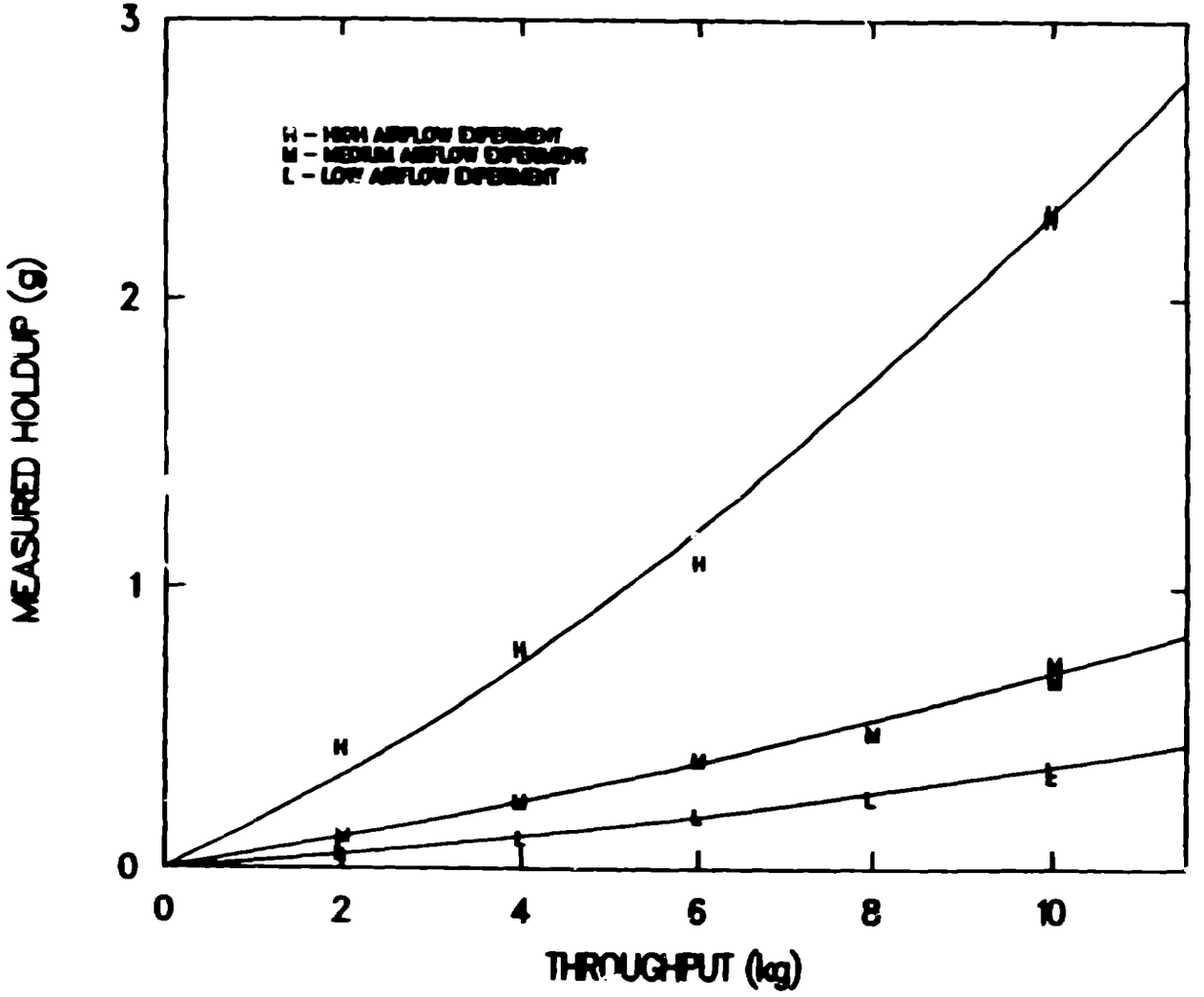

Fig. 5. Data points and models for changes in holdup with air flow rates at the exhaust air filters as a function of throughput of U_3O_8 through the glove box.