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Radioisotope Technology as Applied to Petrochemical Industry

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1. Introduction

Radioisotopes were first applied for industrial problem solving around the middle of the last century. Since then, their use has increased steadily. Today various applications of radioisotopes, as sealed sources and as radiotracers, are well established throughout the world for troubleshooting and optimization of industrial process plants. Petrochemical and chemical process industries are the main users and beneficiaries of the radioisotope technology.

In this chapter we present the three major techniques used in petrochemicals. Gamma-scanning is a very effective non-invasive technique used for on-line troubleshooting of distillation columns and pipes. Neutron backscattering is applied for level and interface detection in storage tanks and other reservoirs. Radiotracers are employed to establish the residence time distribution which is an important mean of analysis of the petrochemical units.

2. Gamma-scanning

Gamma Scanning is the best technique to carry out an internal inspection of distillation columns, vessels and pipes without interrupting production. The gamma-ray scanning technique is widely used for evaluating the operating characteristics of distillation columns considered as the most critical components in petrochemical plants. Gamma-ray scanning provides essential data to optimize the performance of the columns and to identify maintenance requirements.

Gamma Scanning is a very effective, well established, troubleshooting technique. This powerful diagnostic tool, which has been used for decades, has become popular as it allows inspection of the distillation column components without interrupting operation. In comparison to other non-destructive control techniques used in practice, gamma-ray scanning provides, in real time, the clearest vision of the production conditions inside a process reservoir. It is also cost-effective, particularly when compared to lost production (Hills, 2001).

Gamma scanning can help diagnose and solve approximately 70% of column problems encountered at refinery and petrochemical sites. For other cases, it allows resources to be

focused on finding the true source of the problem by eliminating inadequate possible scenarios. It provides essential data to optimize the performance, track any deteriorating effects and identify the maintenance requirements of a distillation column so that it significantly reduces repair downtime (Alami, 2009).

2.1 Main problems met on distillation columns

The hydraulic capacity of trayed distillation columns is always limited by either a high liquid entrainment, or by an overload of downcomers. The technology of high capacity trays deals with these two fundamental limits by reducing the entrainment or by releasing the loads of downcomers. Both are generally connected (Hills, 2001).

2.1.1 Liquid entrainment

The entrainment can be defined as the physical rise of droplets, provoked by the ascending flow of vapour. The vapour tends to hoist droplets upward, while the gravity tends to pull them downward. If the vapour speed is relatively high, then the entrainment can surpass the gravity and some droplets can be transported from a tray to the tray above. The entrainment can be also seen as the excessive accumulation of liquid on trays, which is led by the ascending transport of liquid from a tray to the other one by the current of ascending gas.

A high liquid entrainment can lead directly to a column flooding called "flooding jet". It can also end in it indirectly by increasing the liquid load until reaching the limit of the downcomer, putting in danger the efficiency of separation. Consequently the reflux flow of the column is increased, increasing more the global liquid flow.

The devices of contact between liquid and vapour in the distillation and absorption columns which we meet most generally are trays with sieves and with valves and, in a more or less large extent, of trays with bubble caps. The capacity of retention of these trays is mostly limited by the phenomena of entrainment or flooding. In all the distillation columns of trays type, liquid entrainment and flooding can be present.

2.1.2 Flooding

The flooding of a distillation column is usually defined as the operating mode in which the entrainment is such as there is no downward flow or clear reflux. Conditions of flooding are useful for the engineer-designer, because they represent the maximal authorized operating mode which can serve as reference.

The flooding is usually caused by the accumulation of deposits (dirts) or a blockage on trays. It is also present when the feeding flow of reflux towards the column is upper to the flow coming down from the downcomer.

The flooding can also concern the capacity of downcomers to channel the liquid flow. Because downcomers are passages fitted out for the liquid flow coming down from a tray towards the other one, limitations in their capacity lead to a reduction of the efficiency of trays and, if the limitation is complete, the flooding of the column takes place.

The efficiency of the downcomer or its capacity is limited by:

- Its size
- The difference of pressure between trays, and
- The vapour pulled in the liquid passing by downward.

If the downcomer capacity is inadequate, the level of liquid in this one increases gradually until it limits the liquid flow on the tray above, or on its tray. This, however, increases the entrainment from one tray to the other one and cause finally the flooding. So conditions of flooding can result, either of an inadequate capacity of the downcomer, or of an excessive liquid entrainment in the vapour space.

In summary, the flooding can be seen as an indication of ineffectiveness due to an insufficient liquid-vapour contact (Hills, 2001).

2.1.3 Other encountred problems

Some other problems can be met. These are mainly:

- ''Foaming'': foam formation
- Destruction and collapse of trays
- ''Weeping'' or in other words presence of downward droplets in the vapour space between trays.

2.2 Measurement and physical principles of gamma scanning

In performing a scan of a distillation column or a similar reservoir, a small and adequately sealed source of gamma rays, with an appropriate collimator, is placed on one side of the column and a sensitive radiation detector is placed on the opposite side (Knoll, 2000). A collimated beam of gamma rays passes through the column wall, is affected by the column internals and hydraulic conditions, and passes through the other side. The source and the detector are simultaneously moved down along opposite sides of the column in small increments (Figure 2-1). Guide ropes for the source and detector are sometimes attached to the column to ensure scan orientation and as an additional factor of safety during the scan.
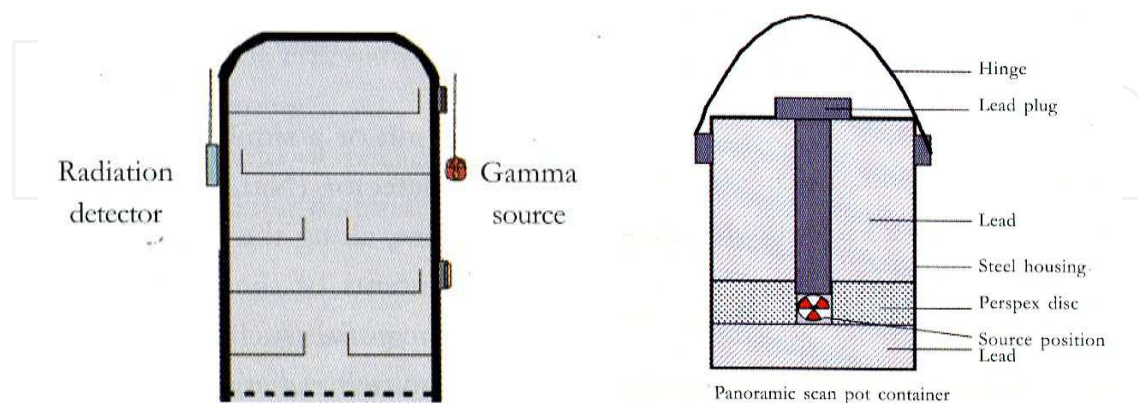

Fig. 2-1. Principle of column gamma scanning.

The scattering of the gamma radiation produces changes in the intensity of the beam that can be correlated to the density of the material inside the inspected column through which the radiation passed according to the following fundamental relationship:

$$I = I_0 e^{-\mu \rho x} \tag{1}$$

where:

- I_0 and I are the initial and transmitted intensities of the gamma beam,
- x is the thickness of the traversed material of density ρ,
- and μ is the coefficient of absorption which is constant for a given gamma-ray energy and material composition.

Equation (1) shows that an increase in material density will reduce the radiation signal and vice versa. The transmitted radiation intensity is measured and recorded via an interfaced portable computer at predetermined length intervals or positions along the side of the column. A radiation absorption profile (the ''scan profile'') is then produced.

By comparing the obtained scan profile with a mechanical drawing of the column, deductions can be pulled concerning, as well the possible mechanical damage of the trays as certain operating conditions of the column, such as flooding, blockages, weeping and other abnormalities of process.

Gamma scanning can be performed on almost any type and size of column (0.5 m to 10 m in diameter) and is not affected by pressure and temperature. It usually requires no preparation of the vessel or alteration to process and can be performed from existing platforms and through insulation on vessels.

The correlation of the changes in density recorded in the scan profile with the inner part of the column lead, therefore, to an accurate picture of performance and physical conditions (Hills, 2001).

Each tray and the space above it reflect its working state. For instance, a tray functioning correctly has a reasonable level of aerated liquid showing a fast decrease of the corresponding density until a clear steam space is reached just below the following tray.

- When gamma radiation goes through a medium containing a tray filled with aerated liquid, much of the incident beam is partially absorbed and the radiation quantity reaching the detector is relatively small.
- When a radiation beam goes through a non-aerated liquid, the majority of this radiation is absorbed and the detected signal is weak.
- When a radiation beam goes through steam, only a small amount of suspended material is present to absorb the radiation. This means that high intensities of radiation are transmitted to the detector.

To sum up, a scan using gamma radiation of a column can detect and localise regions of liquid and steam within the column. It can also discriminate between liquid aeration and can detect levels of foam and aerosol in steam regions (Urbanski, 1999) (Pless, 2002).

For distillation columns, without affecting processing unit, this reliable and accurate technique can be used to determine:

- the liquid level on trays,
- the presence or absence of internals, such as trays, demister pads, packing and distributors

- the extend and position of jet and liquid stack flooding
- the position and the density characteristics of foaming
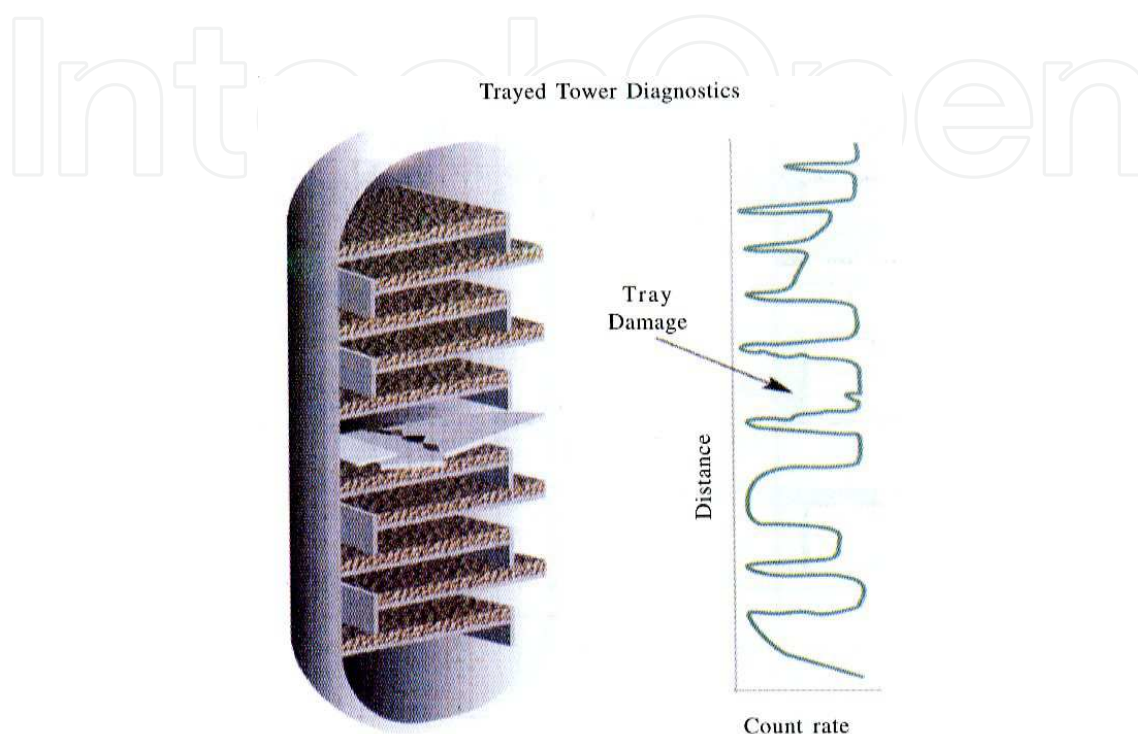- etc…

Fig. 2-2. Typical profile scan obtained (IAEA, 2002).

Baseline Gamma scans are performed after a startup or when a column is running efficiently to define an operational reference condition within the column. The baseline scan can be compared to future scans to determine how the column is responding over time or is responding to changes in operating conditions.

An important factor to take into account is that, as far as is possible, the operating conditions (such as feed rate, temperature and other process parameters) must remain constant especially during the scan investigation. It is very important to record any process changes during the time of the scan. This will facilitate the interpretation of the scan profile if anomalies are observed.

2.3 Scanning of trayed columns

To conduct a tray-column scan, it is advisable to execute a scan across the trays and to avoid scanning through the downcomers of the trays. Typical and recommended scan line orientations for trayed columns are shown in the following figure (IAEA, 2002).
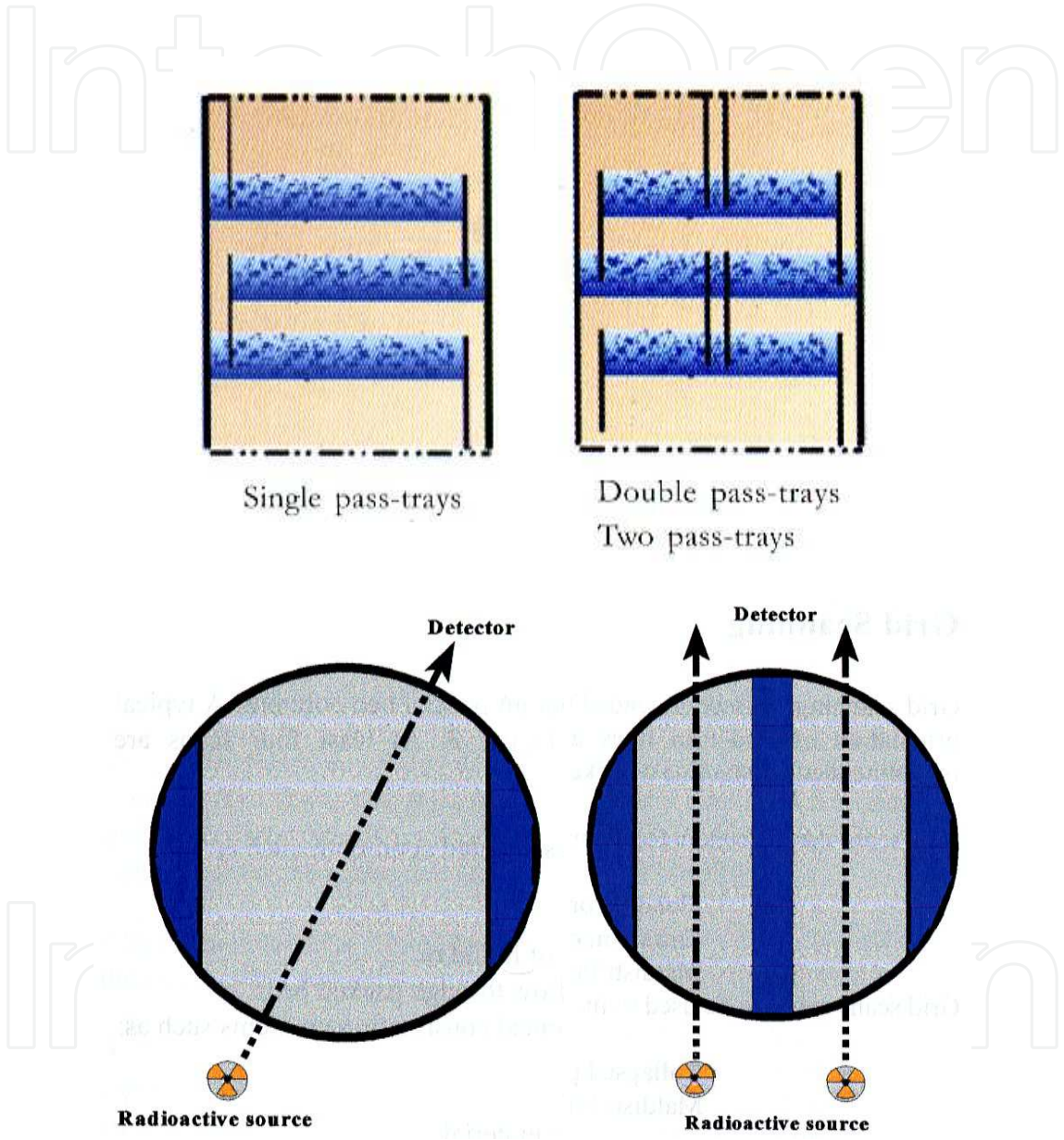
Fig. 2-3. Typical scan line orientation for single pass-trays' column (left) and double pass-tray column (right).

Examples of typical scan profiles obtained for various problems met on distillation columns are presented in Figure 2-4.
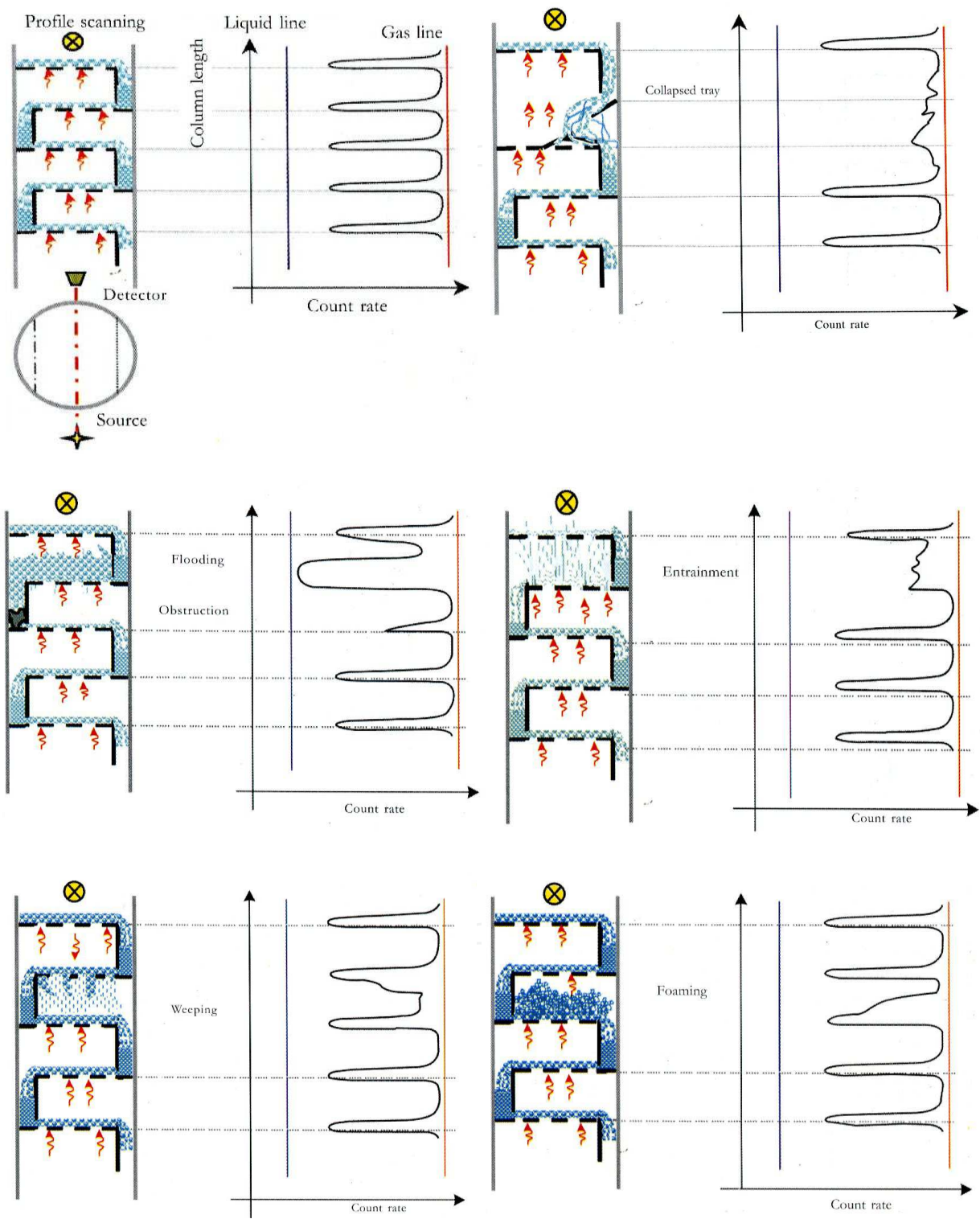

Fig. 2-4. Examples of typical scan profiles obtained for various problems met on distillation columns, respectively from up and left to bottom and right: normal column, collapsed tray, flooding, entrainment, weeping and foaming (IAEA, 2002).

2.4 Scanning of packed beds

Grid scanning is recommended for packed bed columns. A typical orientation of grid scan lines is shown in the figure 2-5. At least four scans are recommended to examine a packed bed column.
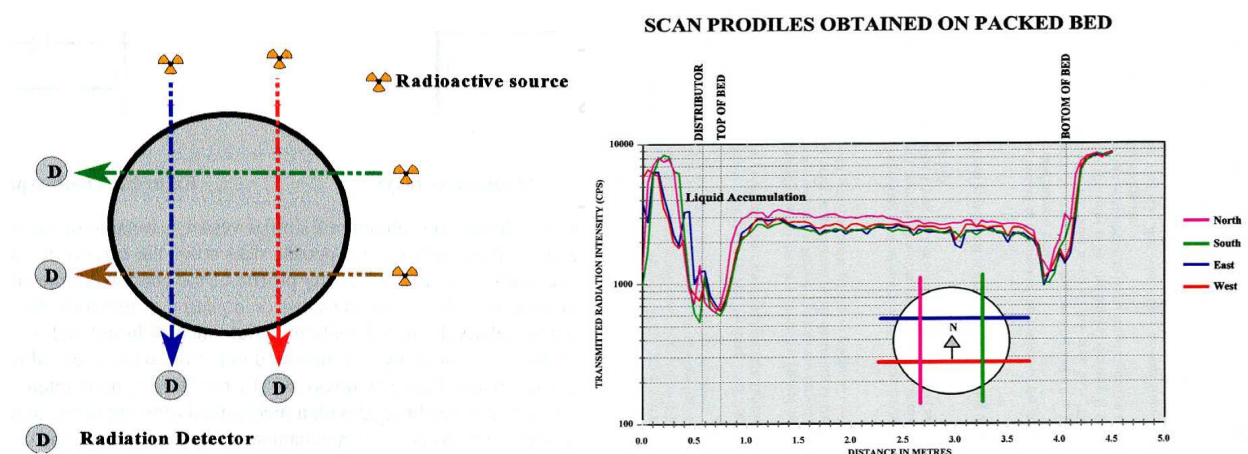

Fig. 2-5. Scan line orientations for packed beds (left) and example of real scan profiles obtained for packed bed (Hills, 2001).

Grid scans may be conducted to investigate process-related conditions such as:

* flooding or blockages
* entrainment or carry over of liquid or
* maldistribution of liquid flow through packed beds.

Grid scans can also be used to investigate mechanical construction problems such as collapsed packed beds or the correct installation of distributors as well as the correct distribution of incoming liquid feed. An irregular distributor can undermine the performance of the entire packed bed and column. Liquid distributors must spread liquid uniformly on top of a bed, resist plugging and fouling, and also provide free space for gas flow. An incorrectly water level installed distributor, that is a tilted distributor, could cause liquid to flow preferentially on one side of the column.

Grid scanning is recommended on packed columns with diameters up to approximately 3m. Larger diameter columns must be approached in a different way, since too large an area (especially in the centre) is not covered.

2.5 Planning of a gamma-ray scan investigation

The following data is required before a scan can be carried out:

* inside diameter and wall thickness of the column (mm)
* bulk density and type of packing material, for packed beds
* downcomer orientation and type of trays present (single, double pass trays)
* operating problems experienced, e.g. low or high pressure problems across the column, or temperature differences along the length of the column

- detailed mechanical drawings of the unit showing internal structure, such as elevations, tray or packing assemblies, nozzle and pipework locations as well as other special features.

Such information is vital for interpreting data from column scan profiles obtained and for identifying and visualising possible mechanical problems. The following additional information is useful:

- gamma scan profiles of an "empty" column (with all the internals but not in operation)
- a scan profile before a maintenance shutdown
- a scan profile after a maintenance shutdown when the column is under normal operating condition.

The activity required depends of the column diameter, ranging from 5-10 mCi for 1-2 m up to 60-70 mCi for 5-6 m and higher for greater diameters. Estimated source strength (activity) can be calculated as follows:

$$A = (D.(d)^2.(2)^{2wt/hl}) / T \qquad (2)$$

Where:

- D = dose rate required (mR/Hr)
- d = diameter of column (m)
- wt = total wall thickness of column (mm) + wall thickness of scan container
- hl = half layer thickness value of material (25 mm for steel for ^{60}Co)
- T = gamma-ray constant for a specific source (1.31 R/h on a distance of 1 meter for 1 Ci ^{60}Co source).

When using the above equation it is suggested that 200 mm be added to the diameter of the column to make provision for the source and detector container on the outside.

The above equation is an approximation, and build-up factors of the material are not taken into account. Shielding calculation software can be used to greater effect.

2.6 Factors Influencing the gamma-ray scanning technique

Major factors influencing the technique are:

- Accessibility to the distillation columns
- External construction of columns (piping, brackets, platforms, etc…)
- Variation of the operating conditions during the scan (feeding flow, temperature, reflux feeding, etc…)
- Weather conditions (wind and rain)

2.7 Pipe scanning

Pipe scanning technique is a derivation of gamma scanning technique for pipes. It can be used to detect:

- solids build-up
- refractory quality and losses

- slugging effects
- vapour and liquid presence in the line.
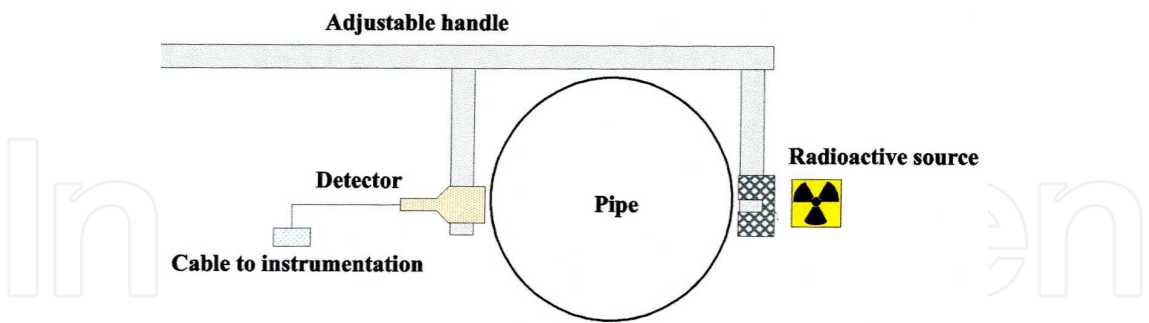
SCHEMATIC DRAWING OF THE PIPE SCANNER

Fig. 2-6. Pipe scanning principle (IAEA, 2002).

There are a number of radioisotope sources, which can be used; two of them are mostly used: [137]Cs with a gamma-ray energy of 662 keV (half-life 30 years), and ^{60}Co with gamma-ray energies of 1172 keV and 1332 keV (half-life 5.27 years). The source activity is calculated accepting a dose rate of approximately 1.0 – 1.5 mR/h, at the detector.

Before executing any pipe scanning, the following information is needed:

- the inside diameter and wall thickness of the pipe
- the medium in the pipe (gas, liquid or slurry).

A jack guide is used so that source and detector can be synchronised and always maintain the same distance. The source must be collimated with a collimator of 6 – 8 mm and 10 mm deep in order to obtain a narrow radiation beam. The detector also must be collimated for best results.

A reference scan is obtained on a representative area of the pipeline that is clean and deposit-free.

Figure 2-7 gives an example of a scan profile obtained for a pipe containing solid deposits. In figure 2-8 scan profiles for various conditions in pipes are presented (IAEA, 2002).
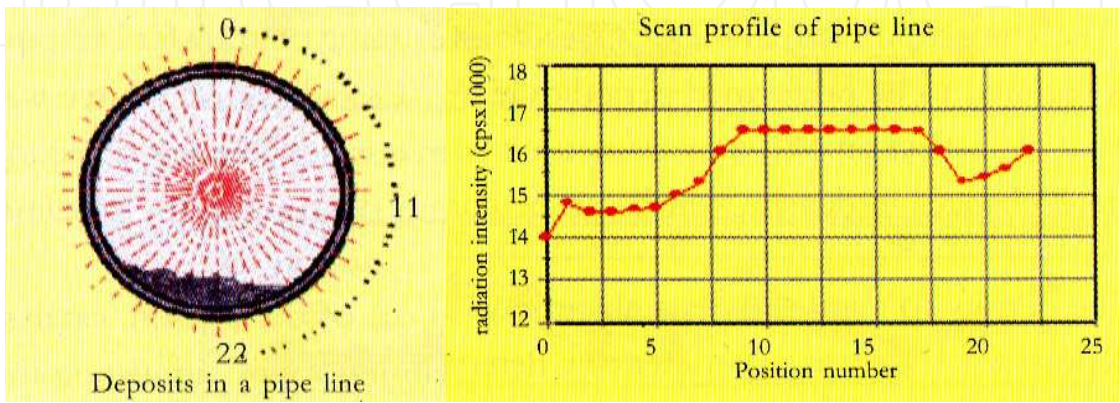

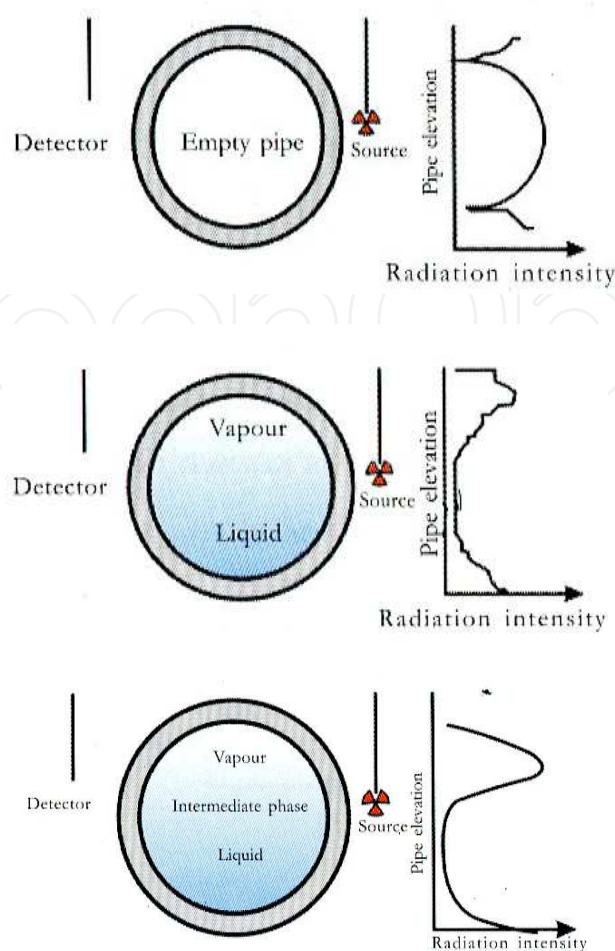Fig. 2-7. Example of a scan profile obtained for a pipe containing deposits.

Fig. 2-8. Typical scan profiles obtained for respectively empty pipe (up), pipe with liquid and vapour (middle) and pipe with liquid and vapour separated by an intermediate phase (bottom).

3. Detection of level and interface by neutron back-scattering technique

Modern petrochemical plant operations often require accurate level measurements of process liquids in production and storage vessels. Although a variety of advanced level indicators are commercially available to meet the demand, these may not suit the specific needs of a situation.

3.1 Neutron backscatter principle

In a neutron backscatter gauge, fast neutrons (with energy 2 to 10 MeV) from a radioactive source (^{241}Am/Be or ^{252}Cf) are beamed onto the inspected vessel. Neutrons are particles with no charge and a relatively large mass. Because the distribution of nucleus is relatively sparse in the matter, it could be assumed, that the neutron radiation can pass deeply enough through the material. The effective measurement volume extends typically 100-150 mm into the vessel. By collision with the nucleus the neutrons lose their energy and change the direction of their movement. For ratio of energy of the neutron before collision E_1 and energy after collision E_2 the relation holds (Thyn, 2002):

$$E_2/E_1 = (A-1)^2/(1+A)^2 \tag{3}$$

Where A is the mass number of atom whose nuclei participated in the collision.

Thus the elements with small atom number have the greatest ability to slow down the neutrons. So, fast neutrons are slowed down mainly by collisions with hydrogen atoms of material inside the vessel (50% of the neutron energy in average is transferred to the hydrogen nucleus in a single collision). The neutron flow has substantially lower energy (thermal neutrons) and different direction after collision with material containing hydrogen. A part of thermal neutrons are then bounced back towards the source. By placing a thermal neutron detector next to the source, these backscattered neutrons can be measured. The number of backscatter neutrons is directly proportional to the concentration of hydrogen atoms in front of the neutron detector. As the source and detector move down the side of the vessel (Figure 3-1), interfaces can be detected thanks to the change in hydrogen atom concentration (Charlton, 1986).
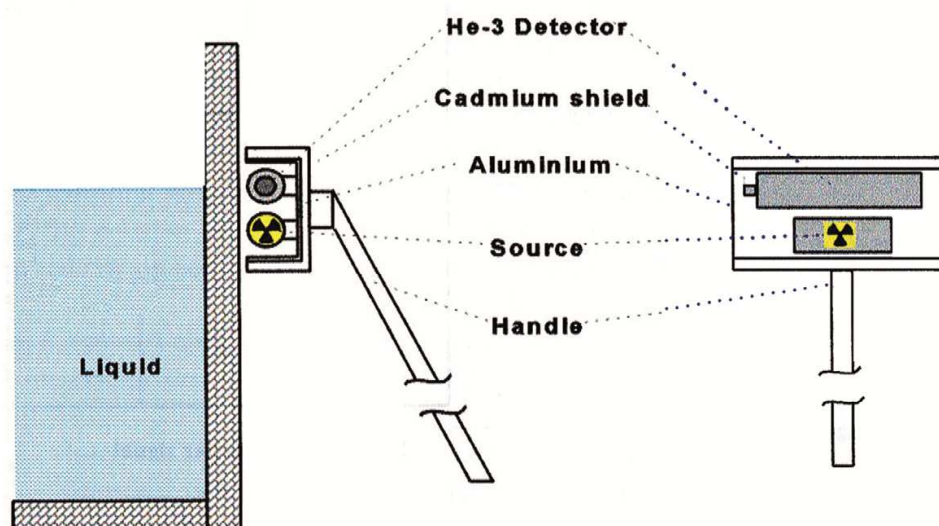

Fig. 3-1. Neutron backscatter level measurement principle (Hills, 2001).

Neutron backscatter gauge clearly indicates solid/liquid and liquid/liquid boundaries and, with careful interpretation of the data, foam levels.

The inspection of the interface between water and oil, as well as among hydrocarbon fractions is the major application of this technique.

Typical profile using the neutron backscattering technique, obtained for a storage tank filled with various liquid and vapour phases, is given in Figure 3-2 (IAEA, 2002).

In practice this method is seldom applied to vessels with wall thickness above 40mm. Although this technique is not suitable in units with thick walls (over 40mm) and although the detector "sees" not deeper than 10 to 15cm into the system, the portable measuring equipment is a valuable tool often used in analysis and diagnostics of chemical processes.

As long as the vessel has a wall thickness less than 100mm, the use of neutrons is a quick and versatile technique, ideally suited if access to both sides of the vessel is not possible.
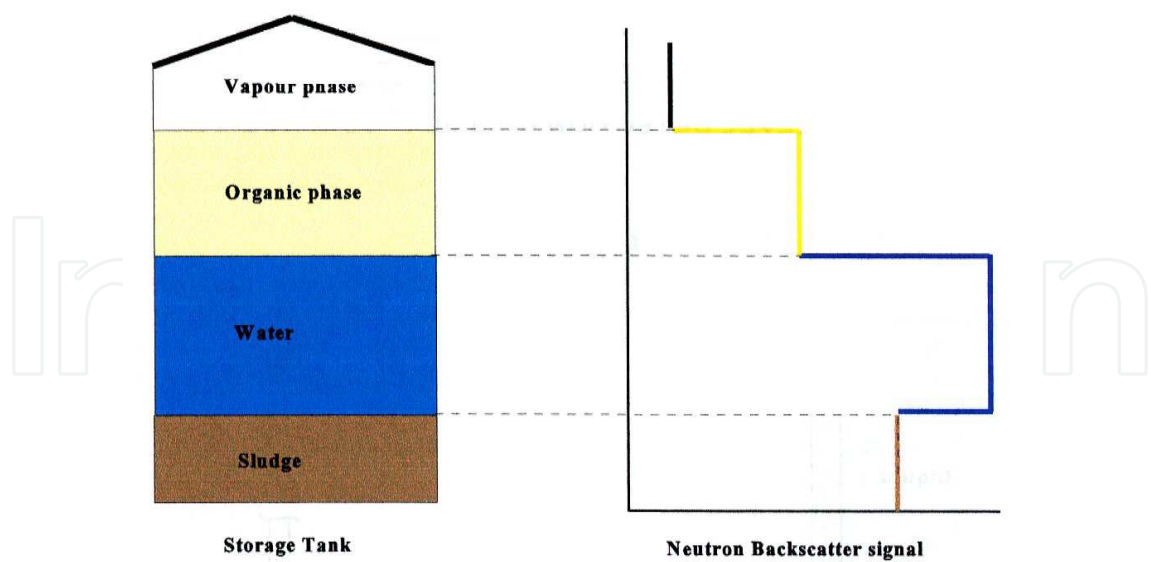
Fig. 3-2. Typical neutron backscattering profile obtained for a storage tank with various liquid and vapour phases.

3.2 Source and detector used

Helium (He-3) or BF3 neutron detectors can be used. He-3 detector has a higher efficiency and is mostly utilized in recent neutron gauges. The neutron source mostly used is 1 Ci ^{241}Am/Be neutron source, which produces a flux of 2.2 x 10^6 n/s with energies from 0.1 MeV to 11.2 MeV, and average energy of approximately 5 MeV. Cf-252 neutron source is used as well, but it is more expensive.

Neutron source	Reaction	Half-life	Neutron Average Energy (MeV)	Flux of fast neutrons
^{241}Am- Be	^{9}Be(α,n)^{12}C	433 y	4.46	2.6 x 10^6 n/Ci/s (0.3 g/Ci)
^{252}Cf	Spontaneous fission	2.645 y	2.1	2.314 x 10^{12} n/(s.g)

Table 1. commonly used neutron sealed sources (Charlton, 1986) (Johansen, 2004) (Martin, 1999).

3.3 Applications and limits

Applications of the neutron backscattering technique include:

- Inventory in oil storage tanks without gauges
- Level determination of liquid petroleum gas storage vessels
- Calibration of permanent conventional level gauges
- Determination of sludge or water layers in tanks
- Measurement of packing levels in absorption towers
- Detecting collapsed beds in packed columns
- Monitoring levels of toxic or corrosive liquids in tank cars and railway tankers

- Identifying build-up and blockages in pipes and reactor coils
- Measurement of catalyst levels in reactors
- Detecting ice formation in flate/vent systems.

Neutron backscatter gauge can be used to measure level and interface of transported liquids in pipes as well.

The following factors may influence the measurement and give wrong results:

- Hydrogen-rich materials in the vicinity of the source and detector but outside the process
- Moisture in insulation
- Non-uniform insulation thickness
- Angle and curved surfaces.

4. Radiotracers applications

The use of the radioactive tracers in industry started about fifty years ago, with the arrival on the market of diverse radioisotopes, and did not, since then, stop knowing a continuous extension. The success of the radiotracers applications is mainly due to the possibility, offered by the unique properties of the radioactive materials, to collect data which cannot be obtained by other techniques of investigation (Margrita, 1983).

The radiotracers allow a diagnosis of the functioning of manufacturing units to reach one of the following objectives:

- to determine the characteristics of circuits: flow rate measurements, leaks on heat exchangers…
- to detect the abnormalities of functioning of reactors: short circuit, dead volume, defective mixture
- Detailed knowledge of the conditions of flow: identification of a mathematical model of the residence time distribution and determination of the characteristic parameters (e.g. Peclet number);
- Define the data to be introduced into the automatic circuits: determination of the transfer functions of phases, substances in solution or in suspension
- Complete the kinetics information by hydrodynamics data: obtaining the residence time distributions of the various phases in reaction.

The importance of such studies is underlined by the fact that the competition to which are subjected the diverse chemical industries brings these to optimize their units' efficiency to make more competitive the made product. A better knowledge of the flow of fluids passing through devices contributes to reach this objective: we are led in certain cases to internal mechanical modifications of the devices which induce an improvement of their performances.

The implementation of radiotracers methods so allows to answer a certain number of questions concerning the characteristics of material transfer in the units without disrupting the operation. The main applications concern very diverse industrial domains such as the oil, the cement, the inorganic chemistry, the chlorine, etc....

Radiotracers play an important role in troubleshooting of processes in petrochemical industry.

4.1 Methodology

4.1.1 What is a tracer?

A tracer is by definition a substance which can become identified with a product, the characteristics of flow of which we want to know. This tracer will have to have a behaviour identical to the product, while being able to be revealed and measured by an appropriate technology.

The used radioactive tracers are generally gamma-ray emitters to be detectable through the walls of the installations by external probes.

These radioactive tracers, so called radiotracer, line up in two categories:

- The tracer is an isotope of the product to be studied; in that case it constitutes the intrinsic tracer so giving the confidence of a physico-chemical behaviour and a hydrodynamics strictly identical to that of the product;
- The tracer is an isotope of an element other than the constituent of the product, when this one can not be or badly activated; in that case we have to make sure that its behaviour is the same than the one of the product to be studied.

The radioactive tracer, obtained by irradiation of some grams of the product in the neutronic flow of a nuclear reactor, is mainly characterized by:

- The period or half-life T (time at the end of which the initial activity is divided by 2),
- The energy of the emitted gamma-rays (E keV),
- The physico-chemical form (gaseous, liquid or solid pulverulent as the case may be).

4.1.2 Why a radioactive tracer? Advantages of the radiotracers

The used tracers are, as the case may be, coloured, fluorescent, radioactive chemicals, etc...

The radioactive tracers present various advantages on the other types of tracers:

- Their qualitative and quantitative detection can be made through walls;
- The ease of qualitative analysis (presence, absence of tracer) or of quantitative of the radioactive tracers, analyze which are independent from the matrix. We shall obtain mostly a maximal quantity of information with a radioactive tracer.
- The radioactive methods offer the widest range of tracers, what is often major when we examine a problem of labelling.
- Another characteristic of the radioactive measures is their high sensitivity. This interesting property finds its origin in the nature of the used detectors, in the fact that in spite of an omnipresent natural activity the signal on noise ratio is favourable, and finally, in the possibility that we have to improve the precision of measure of a sample by increasing the counting time.

The results obtained by this method are interesting during all the duration of evolution of a chemical process since the conception until the exploitation, including the improvement of the installation and the optimization of the operation.

4.1.3 Choice of tracer

The best labelling consists in using radioactive isotopes identical to those of the medium to be marked and under the same chemical form. We then have to deal with an internal tracer. If we do not arrange such isotopes, we shall use an isotope of different nature, so called external tracer. This tracer will be chosen so that we can plan that it will have a dynamic, chemical, physico-chemical behaviour, identical to that of the product to be marked.

- For compounds, mostly under the macro-aggregates form such as powders, the direct irradiation in a flow of thermal neutrons gives rise to radioactive isotopes of often present elements in the state of traces. The sodium, for example, is often used in this purpose.
- If the substance to be marked is made of rather big blocks, we shall make for it holes in which are included the tracers (powder, wire).
- The marking of solid substances is still made by soaking them with solutions of a radioactive substance or by putting down on the surface a radioactive substance.

We are sometimes led to realize, in laboratory, tests the object of which is to show that the proposed tracer is valid.

The gamma rays must have enough energy to get through the wall and be exactly recorded. Its period must be long enough to take into account deadlines between the dates of the irradiation and the use.

Let us indicate finally that the radioactive tracers have, for the used activities, very low masses, of the order of fractions of micro-grams. We often use them, if there are risks of adsorption, in parallel with important quantities (several grams) of similar but not radioactive substances. The last ones are so called "trainers".

4.1.4 General principle of an industrial application of radiotracer

The principle of a tracer experiment is the one of any common method impulse-response (Figure 4-1): injection of a tracer in the entrance of a system and a recording of the concentration-time curve at the exit.

Fig. 4-1. General principle of radiotracer application in industry.

The operation consists in marking a slice of material, in the entrance of the device to be studied and to observe, in various characteristic points of this one, the response curve of the concentration of the tracer versus time, C(t).

1. Injection: the injection of tracers can be realized by various manners: very fast injection, injection with constant flow, injection in a very high-pressure circuit and under diverse

physical forms: gas, liquid, powder. The injection will have to be the most brief possible so that the recorded response in the chosen points of measure can be considered as a Residence Time Distribution (RTD) of the marked phase. The tracer, packaged e.g. in a quartz bulb for gases, is placed in an injection device surrounded with a lead shielding. The injection is made instantaneously in the flow of material in the entrance of the device, by a push of nitrogen the pressure of which is adapted to the operating conditions of the unit.

2. Detection: Detectors allowing to measure through the walls of the installations the gamma rays, emitted by the tracer, are generally scintillation detectors type. The signals delivered by these probes are registered in a data acquisition system, monitored by a computer allowing the storage of the information of about ten sensors (or more) collected at high sampling rate. So, we can have, for every test, of the order of 5 000 information for each measuring channel. Later the data so stored are treated in batch mode by a computer in the laboratory.

4.1.5 What is a Residence Time Distribution (RTD)?

Since its introduction in the chemical engineering by Danckwerts in 1953, the concept of the Residence Time Distribution (RTD) became an important means of analysis of the industrial units. We know that particles crossing a device stay in this one more or less for a long time according to the route which they go through. The Residence Time Distribution (RTD) represents the density of probability which has a particle entering a system, at a given moment, to go out of this system during time. The RTD of the marked phase is calculated from the response curves of the concentration in tracer versus time, C(t), measured in a point of the installation (Guizerix, 1970) (CEA, 1990).

The experimental residence time distribution E(t) is calculated:

$$E(t) = \frac{C(t)}{\int_0^\infty C(t)dt} \tag{4}$$

4.2 Results which can be obtained

The Residence Time Distribution allows to calculate:

- The time of arrival (t_a) which corresponds to the time of transit of the fastest particles between the injection and the point of measure.
- The time (t_m), the abscissa of the maximum of the curve, which indicates the time of transfer of the maximal concentration of tracer.
- The mean residence time, (τ), of the marked product in the system, defined by the difference of the abscissas of the centre of gravity of entrance-exit curves.

The physical parameters directly deductible from the RTD are:

- Speed of the flow of material
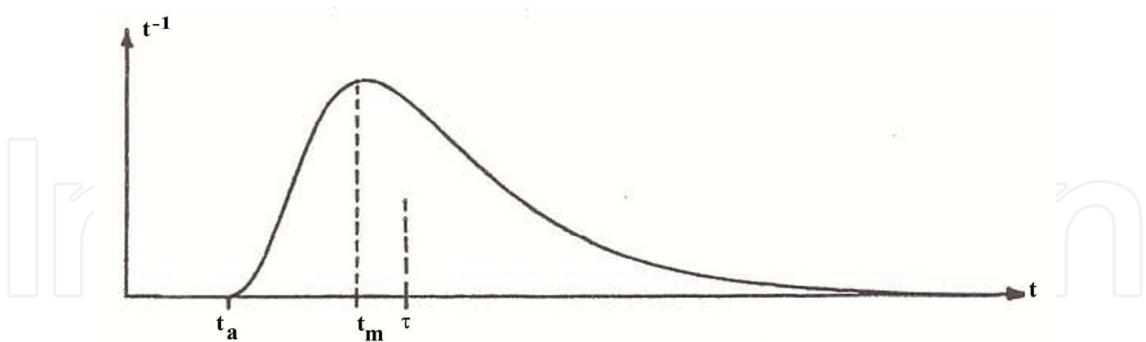- flow of material
- Density

- Dead volumes
- By-pass

Fig. 4-2. Residence Time Distribution (RTD) curve.

4.3 Applications

4.3.1 Flow measurements

The flow measurement represents one of the most ancient applications of the radioactive tracers. According to the cases, two methods are used:

1. Allen's method (or method of "two peaks"), for the pipes of known geometry (figure 4-3): it is the simplest technique where a small quantity of radiotracer is injected in the process and its passage downstream is monitored by two radiation detectors placed outside of the pipe. The used radioisotope should be a Gamma emitter allowing external detection. If the first detector is at a sufficient distance from the injection point, to assure a complete mixture of the tracer, the time measure of transit of the impulse between both detectors allows the calculation of the average speed of flow (speed of the fluid). Knowing the surface of the pipe section, the measured speed can be converted in volumetric flow. This method allows generally measures of average flows with better than ±1 %, when the internal diameter of the pipe is exactly known.
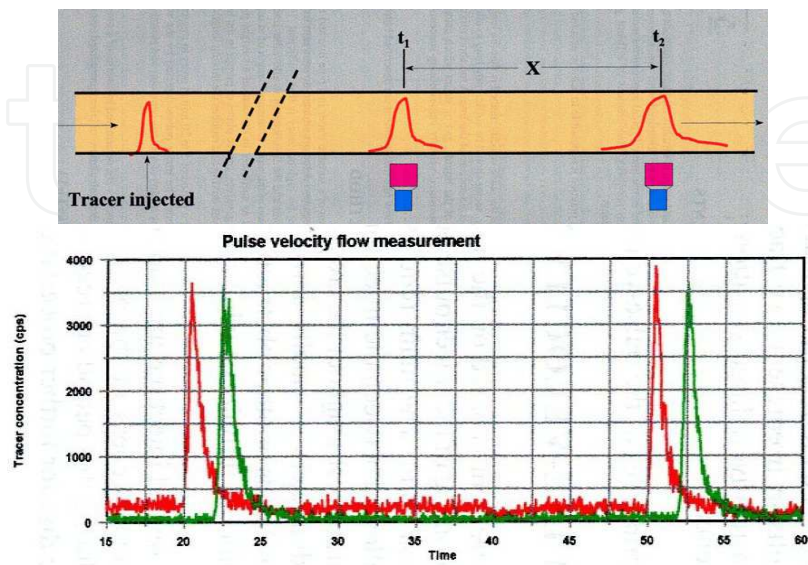

Fig. 4-3. Flow rate measurement by the "two Peaks" or transit time tracer method (IAEA, 2008).

2. The method of dilution, with its two variants: integration method and injection method with constant flow. Here an appropriate radiotracer is injected in the process, and samples are collected in a point enough downstream to assure a complete mixture. The injection of the tracer and its concentration, both in the injected solution and in the diluted samples, are measured. From these data, the flow can be easily calculated.

    a.   Integration Method: the tracer (activity A) is injected during a short interval of time. In a section, situated downstream, we measure in a point the function C(t) representing its passage; the flow is given by:

$$Q = \frac{A}{\int C(t)dt} \tag{5}$$

The good mixing condition is: $\int C(t)dt$ = constant, whatever is the point of sampling in the section of measure.

    b.   Injection method with constant flow: the tracer is injected in a section at constant flow, q, and at a concentration C_0. In a section situated downstream we determine, after reaching a constant regime of concentration, the concentration C of the tracer. If Q is the flow to be measured, an equation of balance of the tracer gives:

$$Q = \frac{C_0}{C \times q} \tag{6}$$

This relation can be written only if the distance between the section of injection and the section of measure is rather big so that in this last one there is good mixture of the tracer, condition which we represent by: C = constant, whatever is the point of sampling in the section. This technique is ideal for the measure of flow in open channels such as sewers and mouths of rivers (the range of measure is very wide: flows of rivers of several thousand cubic meters per second can be measured). The precision is among the best which we can obtain (±1 % or better). A precision of ± 0.5 % can be reached for regular flows with adequate distances of mixture.

These methods of dilution apply (cf. equation of balance) for the measure of constant flows. An analysis can be however made for the application of the method of injection with constant flow in case Q varies. It allows to measure continuously the flow of industrial waste over reference periods, for example of 24 hours.

These methods, apply as well to gases as to liquids, at high or low pressure. The techniques of measure of flow are immediate and are not thus useful for continuous measures. We apply them for the calibration of classic devices (ratemeters), with a 1 % precision, or in the studies of circuits with tapping.

The flows of products (liquid, solid and muddy) or of cooling water are measured in a 1-2 % precision in situations where ratemeters are not installed or are not reliable any more because of problems of deposits or corrosion.

Finally, the implementation of these techniques is very simple and induces only a minimal disturbance of the network; it is need, for example, only of a "pricking" for the injection of the tracer.

4.3.2 Volume measurements: Determination of dead (or stagnant) volumes

The capacity of a device is not always fully used, and it can exist zones, so called dead, which participate little or not in the flow.

The volume of the dead zones is determined by exploiting the obtained residence time distribution (RTD) using the method of dilution which consists in injecting an activity A and in measuring, after homogenization, the resultant concentration, what allows to reach the volume in which diluted the tracer.

The RTD allows to calculate t, the residence time of the material in the device. If τ is the mean residence time, determined by:

$$\tau = \frac{V}{Q} \tag{7}$$

Where V is the volume of the device and Q the flow.

In case the volume is completely occupied, t is equal to the mean residence time τ. If t < τ we deduct generally the existence of a dead volume V_m given by:

$$t = \frac{V - V_m}{Q} \tag{8}$$

Then:

$$V_m = V \times (1 - \frac{\tau}{t}) \tag{9}$$

Exemple de réponse impulsionnelle en présence d'un volume stagnant
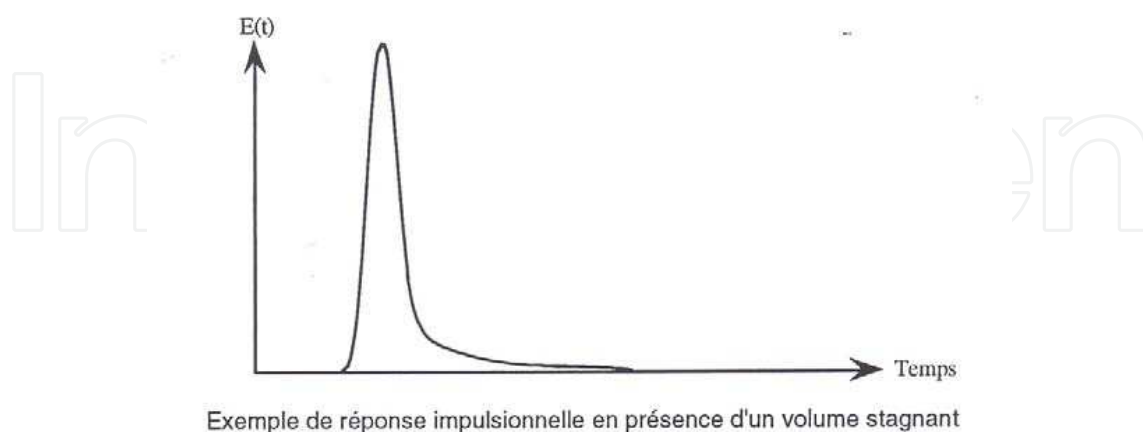
Fig. 4-4. Typical RTD curve obtained in case of dead volume.

The stagnating volume, which corresponds to a zone of fluid little accessible to the main flow, is represented on the impulse response by a trail of the curve.

4.3.3 Leak detection

Leak detection and leak location using radiotracer techniques are probably the most widespread applications of radiotracers in industrial troubleshooting. Leaks create problems in process plants or in pipelines, spoil the quality of the final product or reduce the capacity of oil and gas pipelines and contamination of surface or ground water and soil could also happen (IAEA, 2009) (IAEA, 2004).

The sensitivity inherent to the radiotracers techniques makes them extremely precious for the detection of leaks in pipes, heat exchangers, condensers and valves. The measures are realized while the units stay on operation and without interfering with the process.

Leaks in heat exchangers are more frequent problem in many processing plants of petrochemical industry. Radiotracers are very efficient and most competitive for detecting small leaks inside the heat exchangers. Detection limits of 0.5% of stream flow can be achieved. Radiotracers methods are also very effective when the pipes are buried.

The experiments of leak determination are two types: qualitative or quantitative.

- In the first case, it is only a question of showing that there is a leak between two media. The answer is given by marking the fluid of the first medium and by showing the appearance of the tracer in the second medium.
- In the second case, we try to determine the flow rate of the leak. An injection of tracer is realized in the primary circuit and the impulse responses are measured downstream to both circuits. If the leak exists, some of the tracer will pass into the lower pressure stream. There it will be detected either by sampling the process fluid downstream or by monitoring the movement of the tracer using detectors mounted externally. The equation of balance of the tracer allows easily to calculate the flow rate of leak. Leaks so low as 0.1 % can be measured with online external detection, while sampling can identify leaks as small as 0.01% of the main fluid flow rate.

For leak detection and leak location in buried pipes the so called ''pig technique'' is used. Here the pig means a sensor for detecting and recording radiation signals from inside the pipeline. Radiation detection pig consists of a detector and data logger assembled together inside a compact watertight cylinder. Pig moves inside the pipelines.

The method is a two step procedure. In the first step, radiotracer solution is pumped into the pipeline as a tracer plug without any interrupting operation. Where the ''plug'' meets a hole or fracture, a small amount of the tracer will penetrate and be trapped outside the pipe wall. In the second step, the pig is launched into the pipeline for leak detection run (Fig. 4-5).

This method has a higher sensitivity for leakage detection in underground pipelines as the pig moves in close contact with the leak surrounds. Leaks of the order of 0.1 litter per minute can pinpointed (IAEA, 2009).

4.3.4 Determination of rate of by-pass (short circuit)

We can identify short circuits, i.e. the existence of fluid flows quickly circulating in the reactor. In that case, following an instantaneous injection of tracer, the residence time

distribution (RTD) presents abnormalities of shape due to the presence of a narrow peak coming to overlap in the main response. This means the existence of a preferential passage inside the unit (Fig. 4-6).
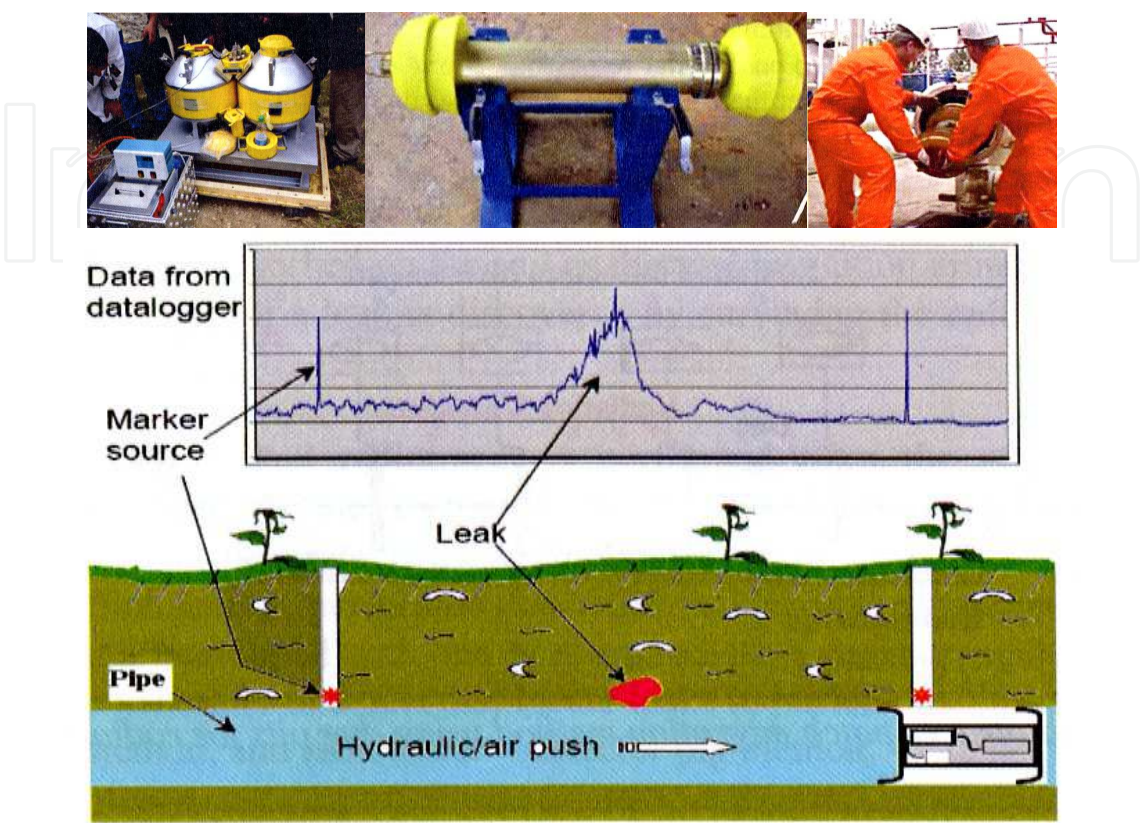

Fig. 4-5. Principle of radiotracer pig method: radiotracer injection device (up, left), pig container (up, middle), pig introduction in pipe (up, right), schematic principle of leak detection in buried pipe (bottom) and typical signal obtained from datalogger (middle).
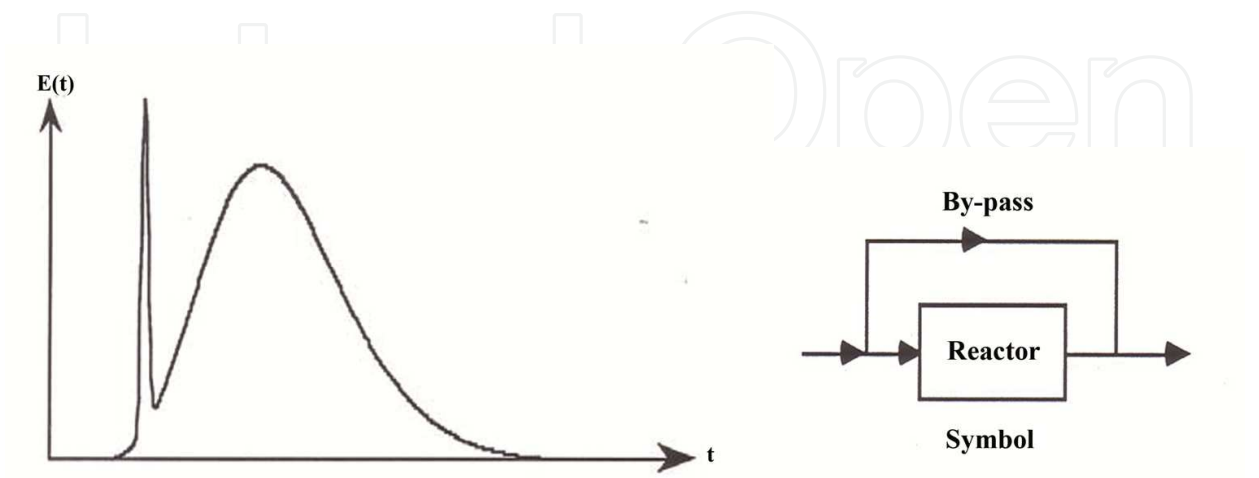

Fig. 4-6. Typical RTD curve obtained in case of by-pass or short circuiting.

The importance of the by-pass can be quantified from the ratio of the area of the peak over the total area of the curve: by interpolating under this peak the main response, we can resolve the impulse response into two responses corresponding to both modes of flow, with respective areas A and B. The rate α of by-pass is (Fig. 4-7):

$$\alpha = \frac{A}{A+B} \tag{10}$$
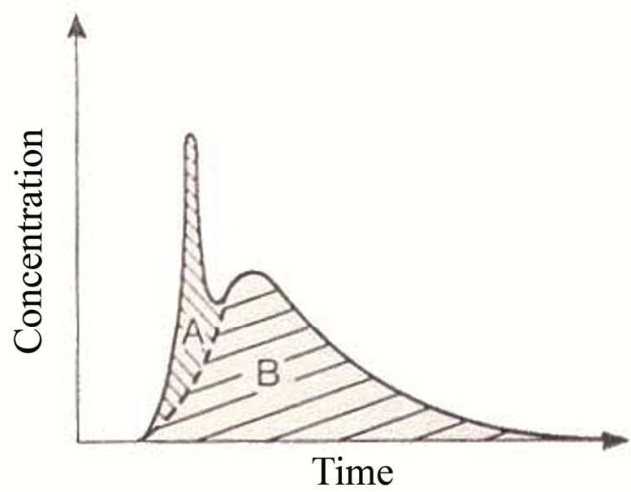
Fig. 4-7. By-pass rate calculation method.

4.3.5 Determination of recycling

The current of recycling corresponds to the reincorporation of a fraction of the outgoing flow, to the entrance of the reactor, and which we can detect on the impulse response by successive, but weakened waves, at regular intervals.
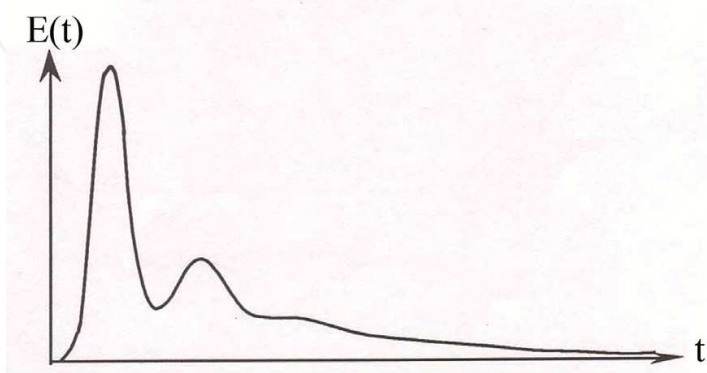
Fig. 4-8. Typical RTD curve obtained in case of recycling.

4.4 Construction, use of physico-mathematical models

One of the most interesting and the most promising modern applications of the tracers, generally, and the radioactive tracers, in particular, concern either the use, or the construction of physico-mathematical models. This is in a general tactics which is always adopted to optimize a situation. Better we know how to describe a phenomenon, more we master it (Margrita, 1983).

4.4.1 Models of flow

The behaviour of the material passing through manufacturing units is very often similar to a type of flow being situated between two extreme behaviours of theoretical flow: "Piston" and "Perfect Mixer".

1. "Piston" model: the fluid moves altogether according to the image of a piston in a cylinder, in parallel slices without any exchange between them. The impulse response of such a system is h (t) = δ (t - τ), δ being a Dirac function (Fig. 4-9).

E(t) : δ(t - τ)

RTD: Dirac impulse delayed by τ

Symbol
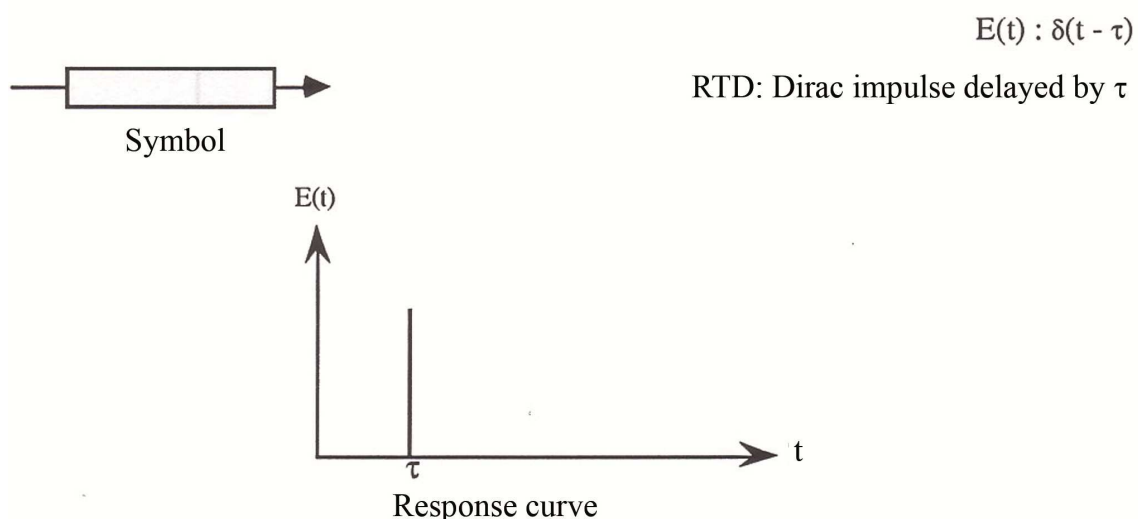
Response curve

Fig. 4-9. Piston model and its response curve.

2. "Perfect Mixer" model: this type of model represents an immediate and uniform mixture of the entering fluid. The impulsive response of such a system is the exponential Shape (Fig. 4-10) and spells:

$$E(t) = \frac{1}{\tau} e^{(-t/\tau)} \tag{11}$$

Symbol

$$E(t) : \frac{1}{\tau} \exp\ (-t/\tau)$$
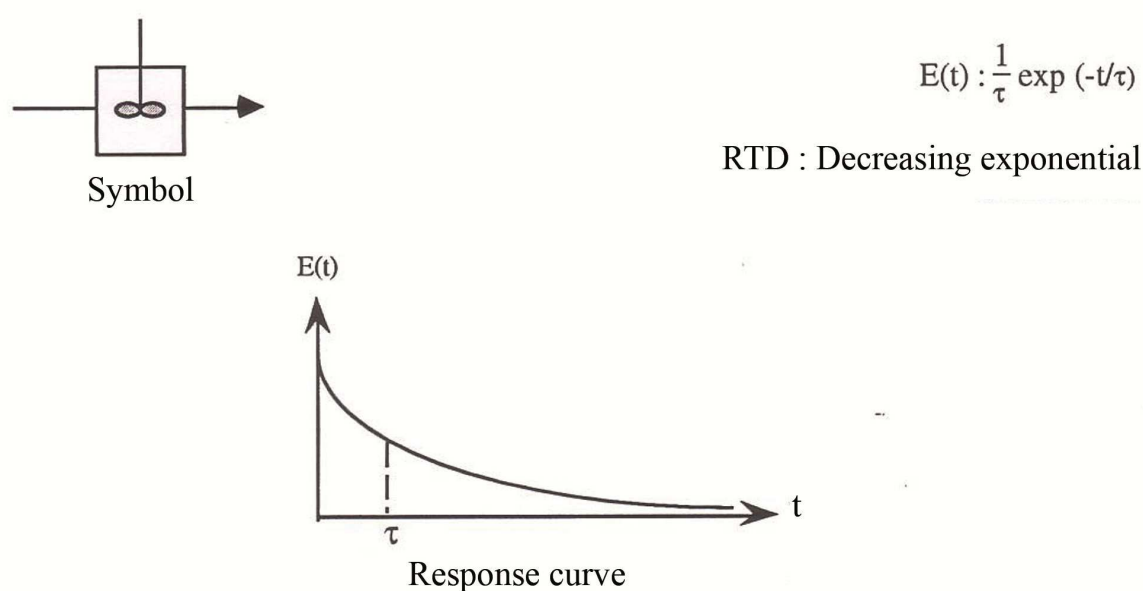
RTD : Decreasing exponential

Response curve

Fig. 4-10. Perfect Mixer model and its response curve.

3. "Piston-Dispersion" model (Fig. 4-11): it is the type of flow that we meet frequently. It is situated between the previous two models. Slices quoted in the "Piston" model exchange some material, leading to a phenomenon of dispersion of this material, quantified by a so called dispersion coefficient. This dispersion is also characterized by a without dimension parameter P called "Peclet Number" and which is calculated by the relation:

$$P = \frac{u \times L}{D} \tag{12}$$

A high value of Peclet number represents a low dispersion. When D→ 0, this model tends towards the Piston model; on the contrary when D → ∞ (big dispersion, P low) this model is comparable to a Perfect Mixer.

The impulsive response has the form:

$$h(t) = \frac{u}{\sqrt{4\pi \times Dt}} e^{-\frac{(L-ut)^2}{4Dt}} \tag{13}$$

"PISTON DISPERSION"

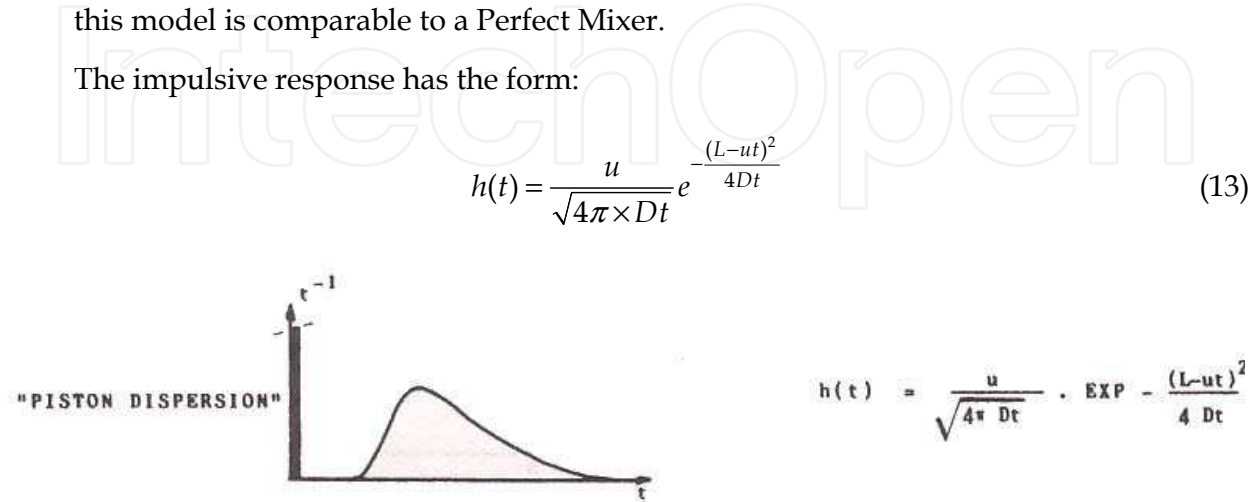$$h(t) = \frac{u}{\sqrt{4\pi\ Dt}} \cdot EXP - \frac{(L-ut)^2}{4\ Dt}$$

Fig. 4-11. Piston-Dispersion model and its response curve.

4.4.2 Identification to a model

The relation between the entrance function and that of the exit of some system is given by a so called Convolution Operation. This operation allows to determine the exit function **s(t)** when we know the entrance function **e(t)** and the impulse response **h(t)** (Fig. 4-12).
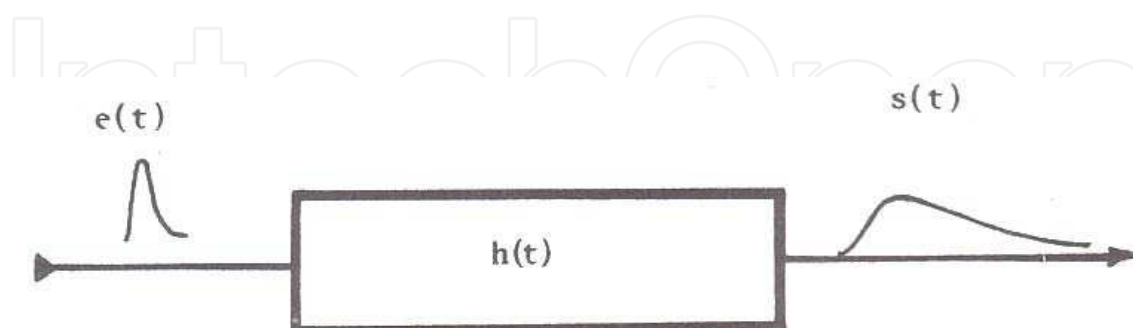

Fig. 4-12.

The fit of a "Piston-Dispersion" model to an experimental curve in exit of a device, consists in determining u and D parameters of the impulse response h(t), in a way that the product of convolution of the entrance function by the impulse response of the considered system, overlaps at best with the experimental curve registered in exit.

The general approach is the following one:

- A physical model of the flow is imagined; its mathematical formulation allows to clarify, according to certain parameters, the residence time distribution.
- A tracer experiment on the unit gives the real residence time distribution.
- A fit between both distributions (experimental and theoretical) by the methods of mathematical optimization allows to evaluate the validity of the proposed model on one hand and to fix the values of the parameters on the other hand.

A good agreement between both distributions means that the proposed model is useful, either to optimize the system, or, still to extrapolate its dimensions to those of another device in project.

The values of the found parameters can be used to the establishment of tables which will facilitate, later, the extrapolations which we have mentioned.

The purpose of fit of a mathematical model can also be the automatic monitoring of the units by computer.

5. Conclusion

The economic benefits that may be derived from the use of radioisotope technology in petrochemical industry are large. In this chapter we tried to present the state-of-the-art in major techniques used in petrochemicals such as gamma-scanning as a diagnostic tool for distillation columns and pipes, neutron backscattering for level and interface detection in

storage tanks and other reservoirs and finally radiotracer applications for troubleshooting and optimizing processes (residence time distribution establishment, flow measurement, dead volume determination, leak detection, short-circuiting or by-pass calculation, etc…). It aims to provide a comprehensive description of what can be achieved by the application of such techniques and to promote their benefits to industrial end-users.

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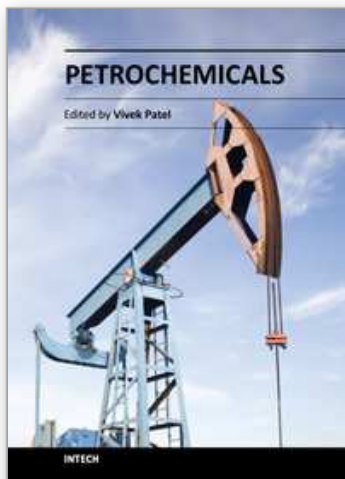
Petrochemicals

Edited by Dr Vivek Patel

The petrochemical industry is an important constituent in our pursuit of economic growth, employment generation and basic needs. It is a huge field that encompasses many commercial chemicals and polymers. This book is designed to help the reader, particularly students and researchers of petroleum science and engineering, understand the mechanics and techniques. The selection of topics addressed and the examples, tables and graphs used to illustrate them are governed, to a large extent, by the fact that this book is aimed primarily at the petroleum science and engineering technologist. This book is must-read material for students, engineers, and researchers working in the petrochemical and petroleum area. It gives a valuable and cost-effective insight into the relevant mechanisms and chemical reactions. The book aims to be concise, self-explanatory and informative.

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