TRACER APPLICATIONS IN PROCESS INDUSTRY

INDUSTRIAL APPLICATION GROUP
Ishak Sajjad
Radiation and Isotope Application Division (RIAD),
Pakistan Institute of Nuclear Science and Technology (PINSTECH),
Post Office. Nilore, Islamabad, Pakistan
Tel: 92-51-9290261; 92-51-2207721; Fax: 92-51-9290275;
E-Mail: sajjad@pinstech.org.pk; or iqbal@pinstech.org.pk

A tracer is a substance whose physical, chemical, atomic or molecular properties can be used to follow its behaviour, movement or concentration in a complicated process. The tracer method usually involves the use of a tracer to label or make easily identifiable a specific phase or part of the system or the traced material. Observation of the behavoiur of the tracer added to a system provides information about the system or part of it. Radioisotopes are widely used as tracers in industry apart from many other disciplines for the reasons that:

- the emission of radiation from a radioisotope is not influenced by physical and chemical condition of the environment or the substance incorporating the radioisotope,
- the detection of radioisotopes is easy with commercially available detectors,
- the sensitivity of detection is high -- enabling the detection of very small concentrations of radiotracer,
- Radioactivity disappears from the system after all nuclides of radiotracer have disintegrated.

Radiotracers are applied across a broad industrial spectrum but the process industry is the major target area. The petroleum, petrochemical, chemical, and mineral processing industries are identified as the most appropriate target beneficiaries of radiotracer applications. These industries are wide spread round the globe and are of considerable economic importance. In the process industry, there are large scale operating continuously. There are huge financial penalties associated with unscheduled shutdowns. The benefits offered by radiotracer technology in terms of on-line fault diagnosis and process optimization are very attractive and the incentive for these industries to apply the technology is clear.

Radiotracers can be applied to investigate many problems in the process industry. Some of the major problems are as follows:

- Leak detection (heat exchangers, pipelines, etc.),
- Homogenization and mixing determination,
- Flow rate measurements,
- Residence Time Distribution (RTD)
- Optimizing Fluidized Catalytic Cracking Units (FCCU's)
- Troubleshooting of process units, etc.

A few case studies are presented regarding the use of radiotracer in process industry.
These case studies were carried out, in various industries, by Radiation and Isotope Application Division (RIAD), Pakistan Institute of Nuclear Science and Technology (PINSTECH), Islamabad, Pakistan.

1. STUDY OF LEAK IN A BATTERY OF HEAT EXCHANGER OF HYDROTREATER AT A REFINERY

Various finished and semi-finished petroleum distillates usually contain perceptible quantities of sulphur compounds, which are undesirable from marketing point of view, and can also interfere in subsequent processing. These sulphur compounds are removed by means of a process known as "hydrotreating". The sulphur is converted into hydrogen sulphide (H_2S) gas by reacting with hydrogen in the presence of catalyst at high temperature and pressure.

At the Pakistan Refinery Ltd., the distillates, which are to be desulphurised, are collected in an overhead vessel and are known as **"hydrotreater charge oi**l" or **"liquid feed"** to the hydrotreater. The liquid feed is pumped from the overhead vessel to a battery of five tubular heat exchangers at a rate of 70 tons per hour through a 25 cm diameter steel pipe of 1.25 cm wall thickness. It enters heat exchanger battery alongwith hydrogen gas from a compressor. Each heat exchanger essentially consists of a tube bundle of about 900 tubes and shell space around the tubes (fig. 1).

The tubular exchanger is about 6.1 m long and 91.5 cm in diameter. In these exchangers the combined feed is pre-heated by the hot reactor effluent in a counter current flow. The combined feed flows through the shell side and reactor effluent through the tubes. The temperature of the feed is about 300 °C when it comes out of the last exchanger and is 80% vaporized. It then enters a furnace where it is completely vaporized at a temperature of about 335 °C. Vaporized feed then enters a reactor. The reactor effluent is hydro-desulphurised product, which flows through the tubes of the aforesaid heat exchangers.

Stations 1 to 5 were situated at the exit of the reactor effluent from each exchanger, station SP.3 at the entrance of labeled oil into the heat exchanger battery and station SR at the exit of reactor effluent from the reactor (figure-1).

Monitoring was started 5 minutes before injection and continued for 40 minutes after the injection as the flow rate data showed that the hydrotreater charge oil would take about half an hour to emerge out of the reactor as desulphurised product after it had entered the heat exchanger battery. Station SR was established to indicate this emergence. Activity was only

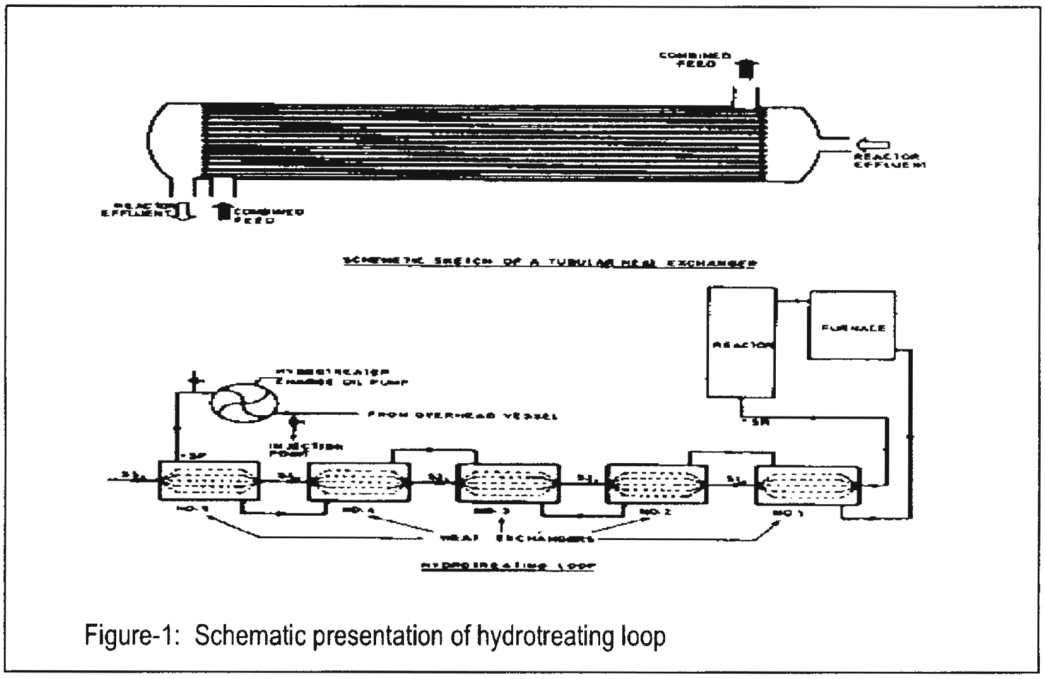

Figure-1: Schematic presentation of hydrotreating loop

A leak was suspected to exist in the tube passes in some of the heat exchangers thereby causing inter-mixing of the liquid feed and the de-sulphurised reactor effluent. Before taking any measures to rectify the system, it was necessary to ascertain the leak and to pinpoint the exchangers in which the leak existed without hampering the production of the refinery. The above mentioned problem was investigated using radioactive tracer technique.

Radioactive tracer ^{82}Br, in the form of para-dibromobenzene was injected into the liquid feed. The injection of the tracer (1.6 Ci) was originally planned for ^{23}rd October at 11 hours but due to some unavoidable circumstances it was made on ^{26}th October at 0325 hours. The activity had by then reduced to about 0.4 Ci. Monitoring was done at five stations established at the desulphurised reactor effluent outlets from each exchanger, at the liquid feed inlet of exchanger No. 5 and at the reactor outlet. detected at station 5 as shown in figure 2. The peak at 1.1 minute is due to the instantaneous rise in the background on the arrival of tracer pulse; however, the peak at 2.3 minute indicate the activity due to the leakage in heat exchange No. 5. The data obtained for the remaining four heat exchangers is shown if figure-3. inconclusive as the tracer activity was considerably reduced due to delayed, prolonged and uncontrolled injection of the tracer.

2. LEAKAGE INVESTIGATION IN A VERTICAL HEAT EXCHANGER AT A REFINERY USING RADIOACTIVE TACER TECHNIQUE

The finished product (Hi-Octane) from the Plateforming Combined Feed Exchanger (Texas Tower) at a Refinery was not up to the mark due to suspected leak in the unit. The main function

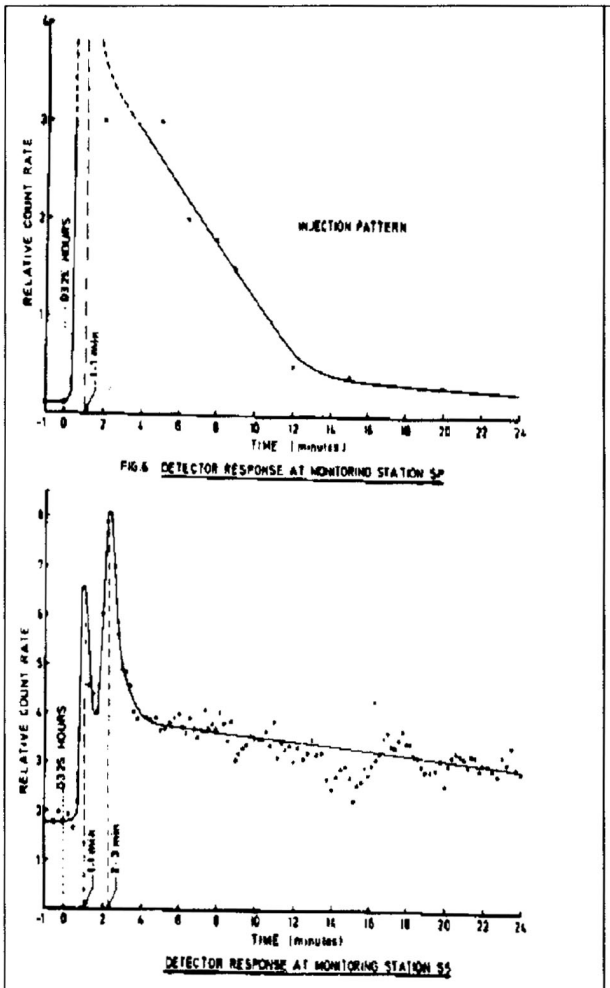

Figure-2: Detector response at monitoring station SP and station S5

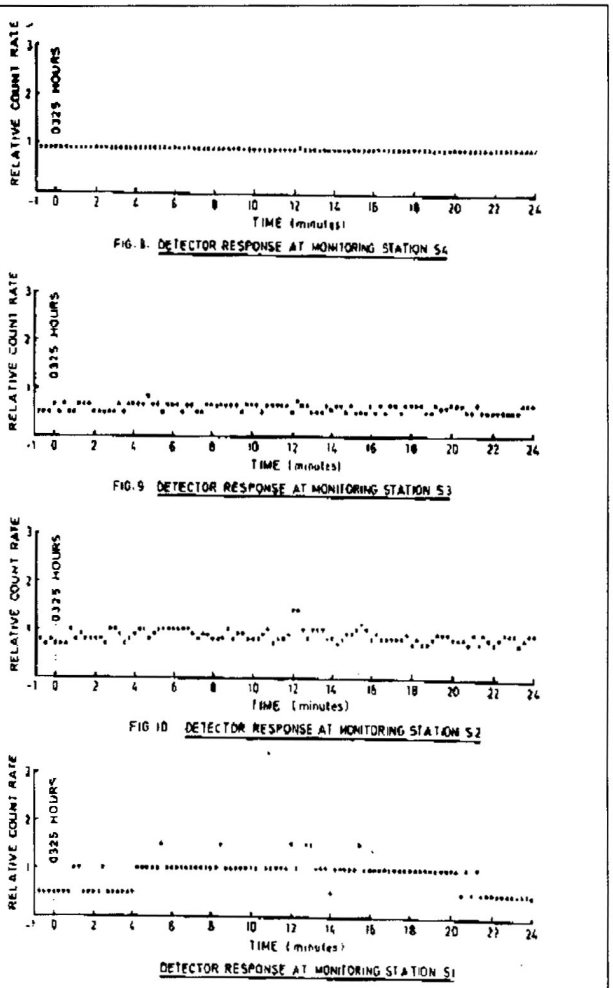

Figure-3: Detector response at monitoring stations S1 to S4

of the unit is to heat the incoming fluid. The heat exchanger is 25 meter high with usual operating pressure of 26.8 Kg/cm 2 (485 psig) in tube side. Neptha plus hydrogen is the fluid in the tube side and Hi-Octane (finished product) in the shell side. The flow of fluid is about 150 barrels per hour. The fluid in tube side is bound for cascade of the furnaces for further heating and catalytic reactor for further processing. The leak could not be identified with the instrumentation and methods available at the refinery. For this study, radioactive bromine-82 in the form of Para-Di-Bromo Benzene (1,4 Di-Bromo Benzene) was prepared at the PINSTECH reactor and transported to NRL Karachi. An injection point close to the main pump/suction header was used to introduce the radioactivity into the system. Flow of this feed passes through tube section of the heat exchanger and enters plateformer charge heater (furnace) and plate former reactor-1 (catalytic reactor).

About 500 mCi of radioactivity was introduced at the injection point. This activity was detected at the radiation detection station just before the tube inlet. Activity was also appeared at the radiation detection point at inlet of plateformer charge heater and also at the inlet of plateformer ractor-1 (figure-4). However this activity was not detected at the outlet of this reactor. This means that the radioactive compound was adsorbed/absorbed in the reactor. Hence it was observed that once the activity reached the reactor, it disappeared from the flow. The tracer activity was detected at the shell outlet after some time. As the activity reaching the reactor is disappeared from the flow, the presence of activity at shell outlet means that there is a (definite) leakage in the heat exchanger.

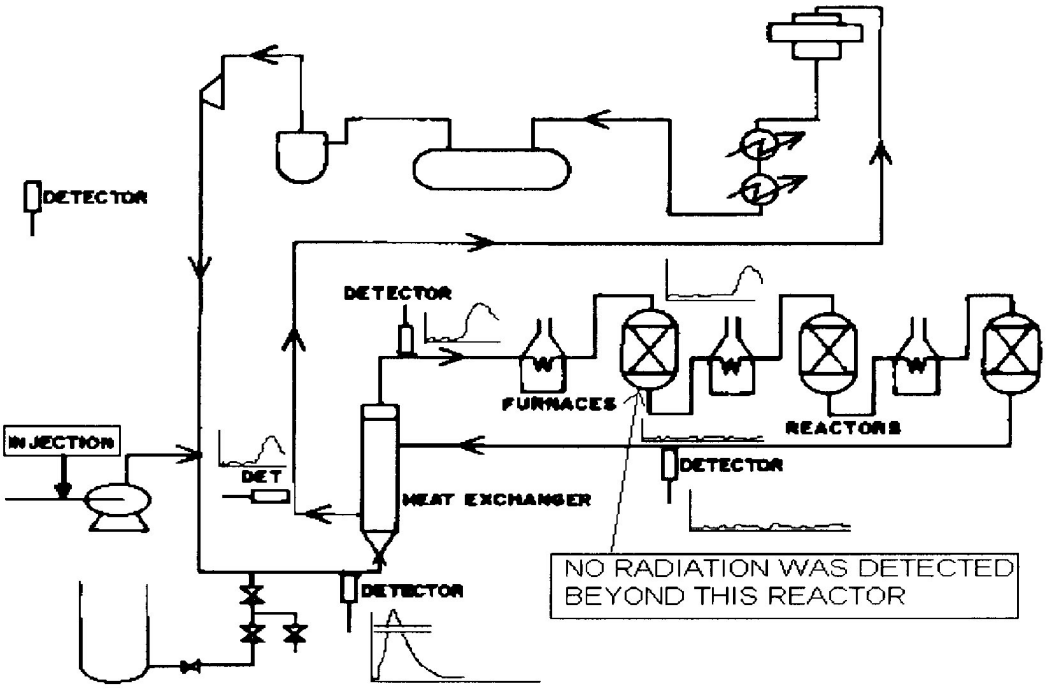

Figure-4: Schematic presentation of a Platformer of refining process

3. TRACING OF A SCRAPER PIG DURING CLEANING OPERATION OF AN UNDERGROUND PIPELINE

Underground pipelines are usually laid for the transportation of different fluids like aviation fuel, gasoline, naphtha etc. from one place to the other. Such pipelines, before being commissioned, are cleaned thoroughly by flushing with water and solvents and by passing scraper and brush pigs. During the cleaning, there is a possibility of the scraper pig getting stuck due to any defective bend, excess welding beads or excessive debris accumulated ahead of it. In such an event the stuck pig is to be located before any measures can be taken to release it. This can be conveniently done by tagging the pig with a radioactive source. In the presence of the radioactive source the scraper can be located wit the help of an appropriate radiation detection system.

A radioactive tracer (sealed source) was used during the cleaning operation of a 17 km long refinery-airport pipeline. The route map of the pipeline is shown in figure 5. The pipeline had, on the average, 1.35 meter of earth cover. The scraper pig, tagged with 200 mCi Co-60 radioactive source, was launched into the pipeline from the refinery-end under hydrostatic pressure. Sixteen monitoring stations were established to record the passage of the scraper across these points.

The speed of the scraper in the pipeline was not high and two teams carrying mobile radiation detection systems monitored the passage of the scraper at alternate stations. The scraper got struck during the first passage. Its passage was recorded at all the stations from 1 to 5 but not beyond 5 indicating that it had stuck somewhere **between station 5 and 6.** The section of the pipeline between these two stations was scanned from above the ground using portable radiation detection set up. The scraper was located at point E close to station 6 (figure 5). The soil cover was removed and the portion of the pipe uncovered. By opening the flange F, increasing the hydraulic pressure at refinery-end and gently hammering the pipe where the pig got stuck, did help the scraper come out of the pipeline with lot of scrap ahead of it. The scraper and brush pigs were passed through this section a number of times. The flange F was then joined and the entire length of the pipeline was cleaned with the pigs. **Necessary precautions were strictly observed at all stages of the experiment to avoid any possible health hazard**s. The experience of tagging the scraper with a radioisotope during the cleaning operations of the pipeline has been very successful. The use of radioisotopes in other similar operations is recommended.

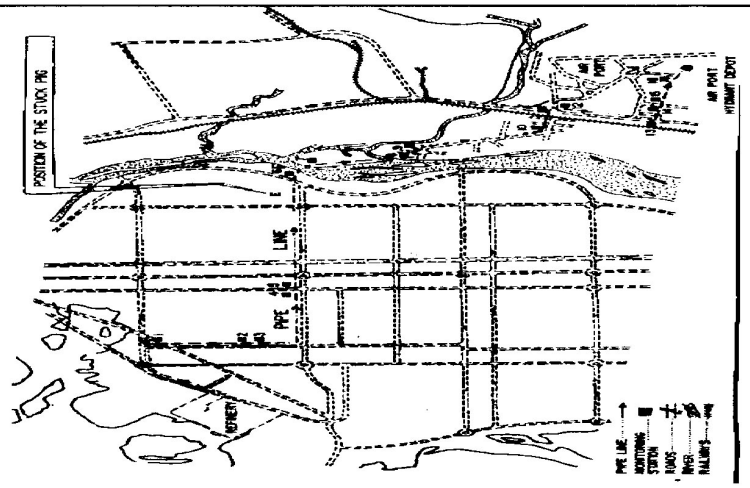

Figure-5: Route map of airport-refinery pipeline

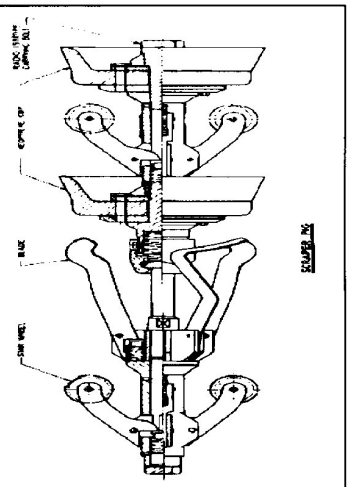

Figure 6: Scraper Pig used for pipeline cleaning

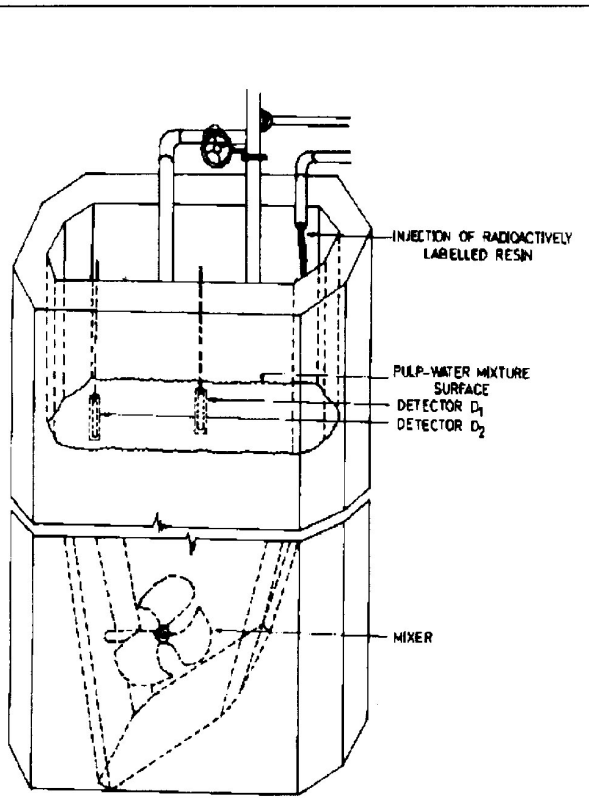

Figure-7: Schematic showing mixing time experiment in the pulp chest

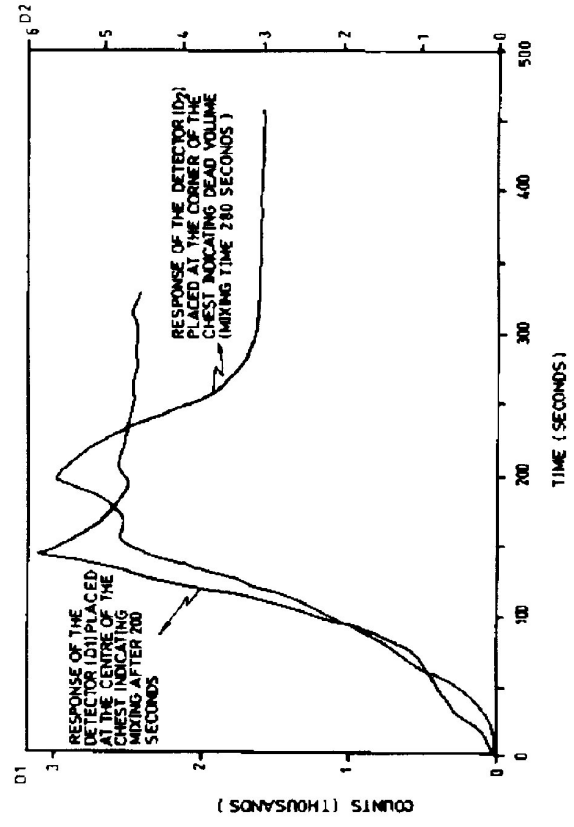

Figure-8: Response of two detectors at two different positions in the pulp chest

4. DETERMINATION OF MIXING TIME OF ROSIN IN THE PULP CHEST OF A PAPER MAKING PLANT

Mixing time of rosin (chemical) in a batch process of paper making plant was determined using radiotracer technique. The raw material for the chest is pulp, which is derived mostly from kachi grass, bagasse and waste paper through digesters. Usually, the chest (figure-7) is filled with a mixture of 1.2 metric tons of pulp and 34 tons of water. To optimize the characteristics of the pulp, solutions of 20 kg of rosin, 80 kg of soap stone powder and 48 kg of alum are added one after the other. During this process, a propeller located at the bottom of the chest (figure-7) vigorously agitates the mixture of the chest solution. For the experiment, 370 MBq. of 99m Tc saline solution was injected in the pulp chest. Radiation detection was carried out at two pints i.e., in the centre and on a side (far side of the injection point) of the chest.

The experimental results (figure-8) revealed that the rosin pulp mixture required only about 5 minutes to achieve a desired level of homogeneity. This mixing time is four times less than the routine mixing time. The results also showed a dead volume effect.

5. LEAKAGE DETECTION IN EXCHANGER AT NATIONAL REFINERY, KARACHI

A Radiotracer Test was conducted, by PINSTECH Team, at National Refinery Limited (NRL), Karachi on 11-01-2001. The Leak Test was carried out in Exchanger Unit (103-E-6). A Radiotracer Br-82 in the form of Di-Bromo-Benzen with an activity of 130 mili Curi was used. A brief feasibility of experimental set up was carried out and background radiation levels were recorded before tracer injection. Special arrangements were made to inject Radiotracer in the system. Following monitoring stations were set up to monitor the passage of Radiotracer in the Exchanger loop. The relative positions of various detectors are shown in figure-1.

Detector-1: At the Tube Inlet --- Just before the tube inlet pipe enters the exchanger
Detector-2: At the tube outlet --- Away from the Exchanger
Detector-3: At the Shell Inlet --- Away from the Exchanger
Detector-4: At the Shell Outlet --- Just after the shell outlet pipe goes away from the Exchanger
Detector-5: At first Platform (near Shell Top) --- against the Shell wall

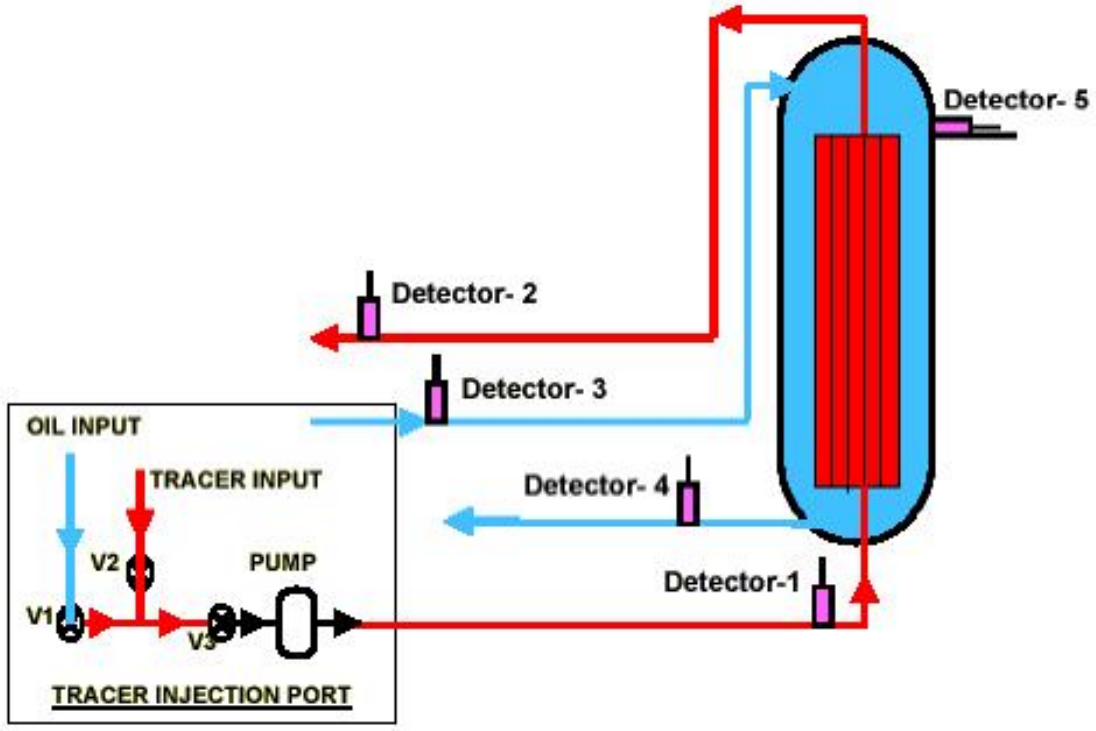

Figure-1: Schematics of Experimental Set-up showing Tracer Injection Port and position of various detectors.

All the Ratemeters and Computer were time synchronized. Data recording was started at 14:23 hours. The detector-4 placed at Shell outlet to monitor leakage was connected to computer for data acquisition. The data from other detectors was recorded manually. The data of detector-4 was also recorded manually to avoid data loss in case of any problem with the computer. Data of detector-4 was recorded every 5 seconds while for other detectors, data was recorded for every 10 seconds.

Tracer Injection: Valves **V-1** and **V-3** of the Injection Port (see figure-1) were closed. The Flange at the top of valve **V-2** was removed and the valve **V-2** was opened. The oil level in the horizontal pipe between valve V-1 and V-3 was maintained such that 3/4 of pipe diameter was filled with oil. Specially designed device to crush the silica glass ampoule was inserted vertically in the pipe through valve **V**-2. Two glass ampoules containing Radiotracer Br-82 (in the form of Di-Bromo-Benzen powder) were inserted in the crushing device. Ampoules were crushed and tracer was mixed in oil in the pipe. The ampoule-crushing device was rinsed (inside the pipe) with inactive oil before it was taken out and stored safely. The valve **V-2** was closed and Valves **V-3** and **V-1** were opened. The Radiotracer was injected into the system by starting the pump.

The injection was made at 14:32 hours on 11-01-2001 in the Tube inlet pipe through Injection Port as described above. The data was recorded from 1423 to 1600 hours on 11-01-2001 (i.e. for 1 hour & 37 minutes). Data was analyzed and plotted as shown in figurer-2, 3, 4 & 5.

Discussion and Results

The data obtained from detector-1,2,4 & 5 is plotted in figure-2. As the Radiotracer did not appear at detector-3, its data is not plotted. The data from detector-4 with 5-second time base is plotted in figure-3. The data from detector-1 and detector-4 is plotted in figure-4. The zoom view of figure-4 near the peak area is shown in figure-5. The timings of tracer-peak arrival and peak duration are also given in figure-2 and figure-5.

The data from detector-1 (monitoring tracer injection in tube inlet) and detector-4 (monitoring leakage, if any, in shell outlet is very important and is to be analyzed carefully. Tracer injection was made away from detector-1 at 14:32 hours. The tracer plume of injection reached detector-1 at 14:33:50 hours and the tracer plume passed detector-1 at 14:34:50 with a duration of 60 seconds The maxima of injection peak was recorded at 14:34:00 hours (please see peak-B, figure-4 & 5). A tracer peak was also recorded by detector-4 placed at shell outlet. The tracer peak arrived at detector-4 at 14:33:05 hours and passed away at 14:34:05 hours with 60-second duration. The maxima of the peak was recorded at 14:33:15 hours (please see peak-A, figure-4 & 5). The detector-1 and detector-4 recorded the peak for the same duration i.e., for 60 seconds and the peak maxima reached within 10 seconds of the arrival of tracer peaks on both detectors. **However, detector- 4 recorded the tracer peak 45 seconds earlier than detector-1**. That means detector-4 recorded tracer peak before the tracer entered the exchanger. This indicates that the peak recorded by detector-4 at 14:33:05 hours is not related to any leakage in the exchanger but this peak is due the fact that detector-4 has seen activity of injection plume while tracer passed through the tube inlet pipe in the near vicinity (see figure-1). The detector-5 placed against the shell wall, at the platform near the shell top (see figure-1) recorded tracer peak maxima at 14:37:10 hours while the detector-2 placed against tube outlet (see figure-1) recorded the peak maxima at 15:08:10 hours. The data acquisition was continued for 1 hour and 37 minutes after the tracer injection, but detector-4 did not record any leakage. The absence of any tracer at detector-3 placed at shell inlet (see figure-1) shows that tracer is diluted and adsorbed somewhere in series of reactors and did not appear afterwards at the shell inlet.

RESULT: The Tracer Test reveals that there is NO LEAKAGE in the Exchanger.

Radiation Safety Aspects

All necessary radiation protection aspects were taken into account during all stages of the experiment (radioisotope production, transportation, injection, etc.). Nobody except PINSTECH personnel was allowed to stay within 10 meters diameter around the injection port during tracer injection till the area was checked at the end of experiment. The injection port and the area around were checked and no radiation contamination was found. However, there was still little activity inside the pipe at the injection port and that too was safe at 1 meter distance. The process engineer at site, his staff and Inspection Engineer were briefed about the necessary precautions in this regard. Next day (12-1-2001), PINSTECH team checked injection port again and radiation level was found within safe limits. No radioactivity was recorded by Detector-3 placed at the shell inlet. That means that there is no question of any radioactivity in the refined product.

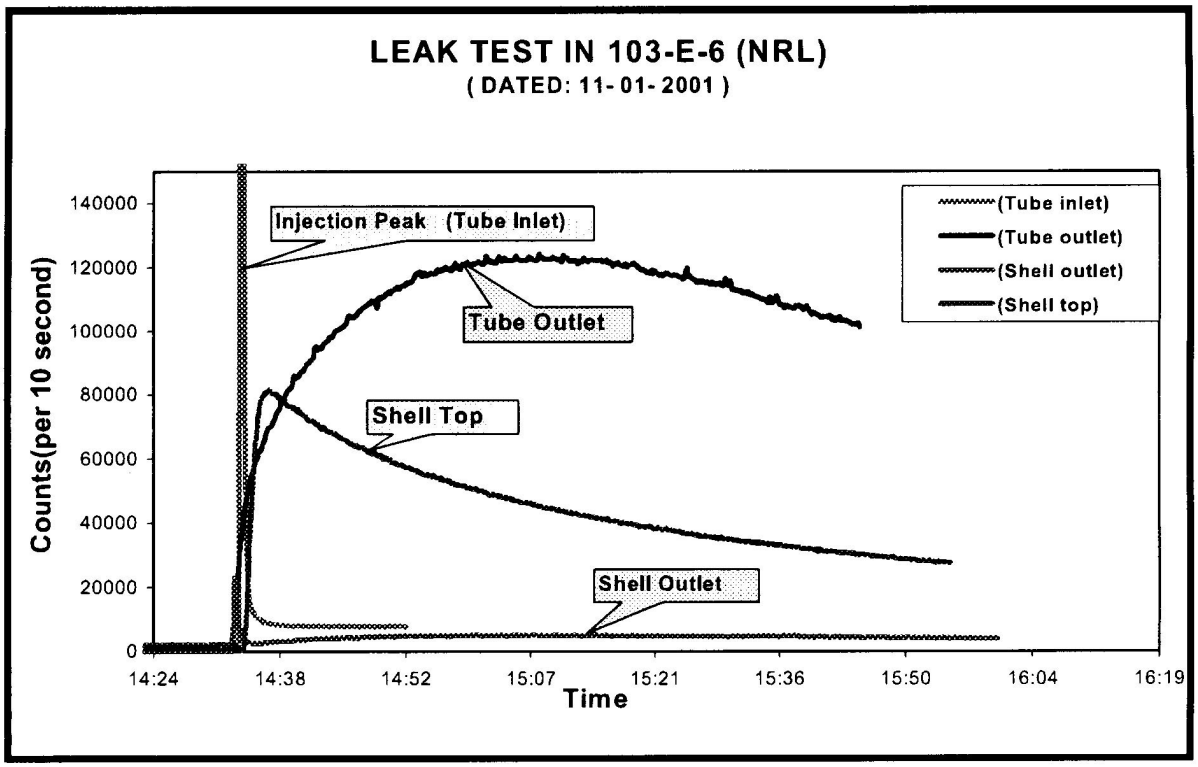

FIGURE-2: Response of Detectors 1, 2, 4 and 5 with 10 second counting time

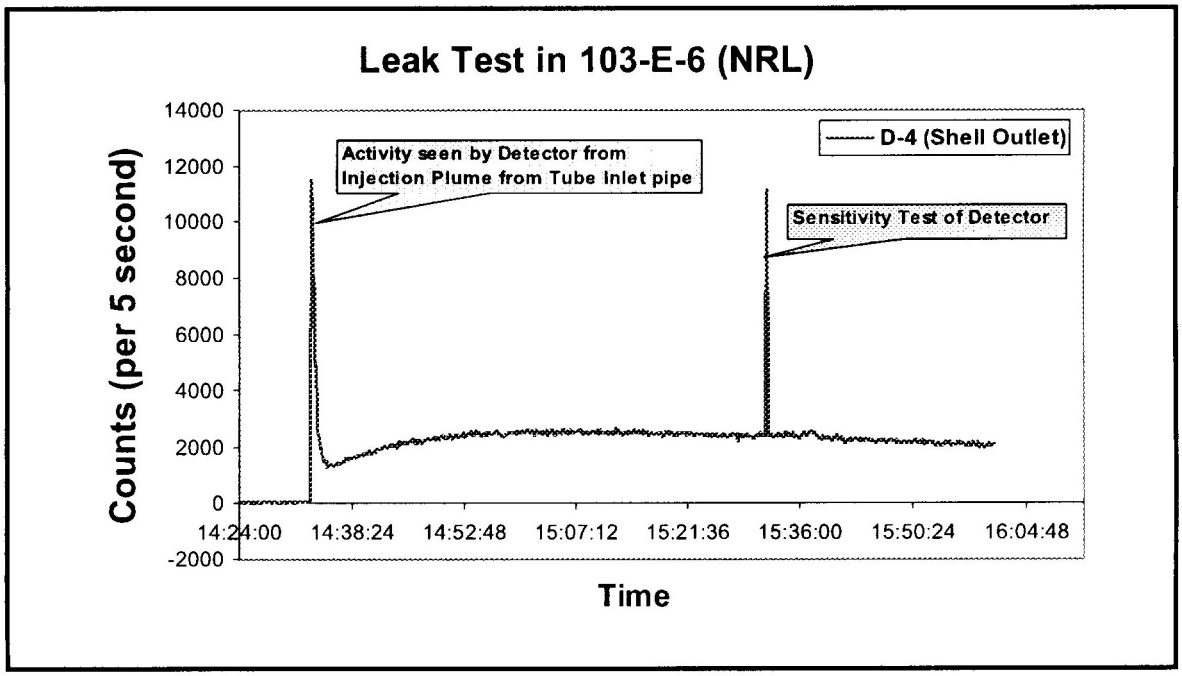

FIGURE-3: Response of Detectors No. 4 with 5-second counting time

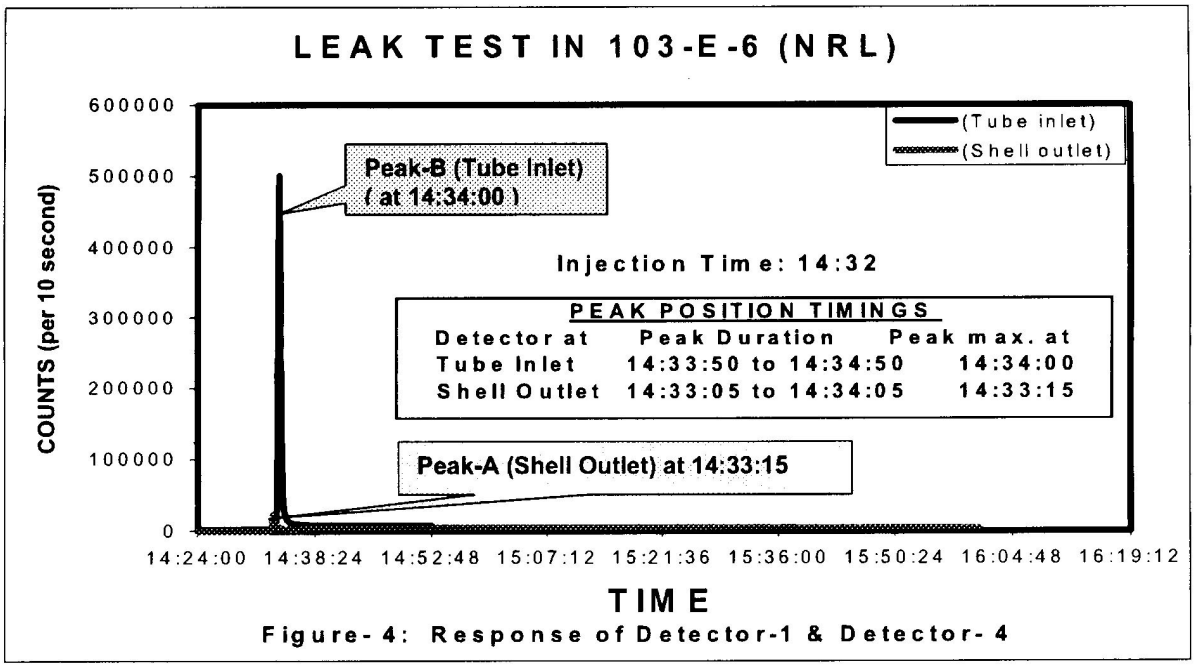

Figure- 4: Response of Detector-1 & Detector- 4

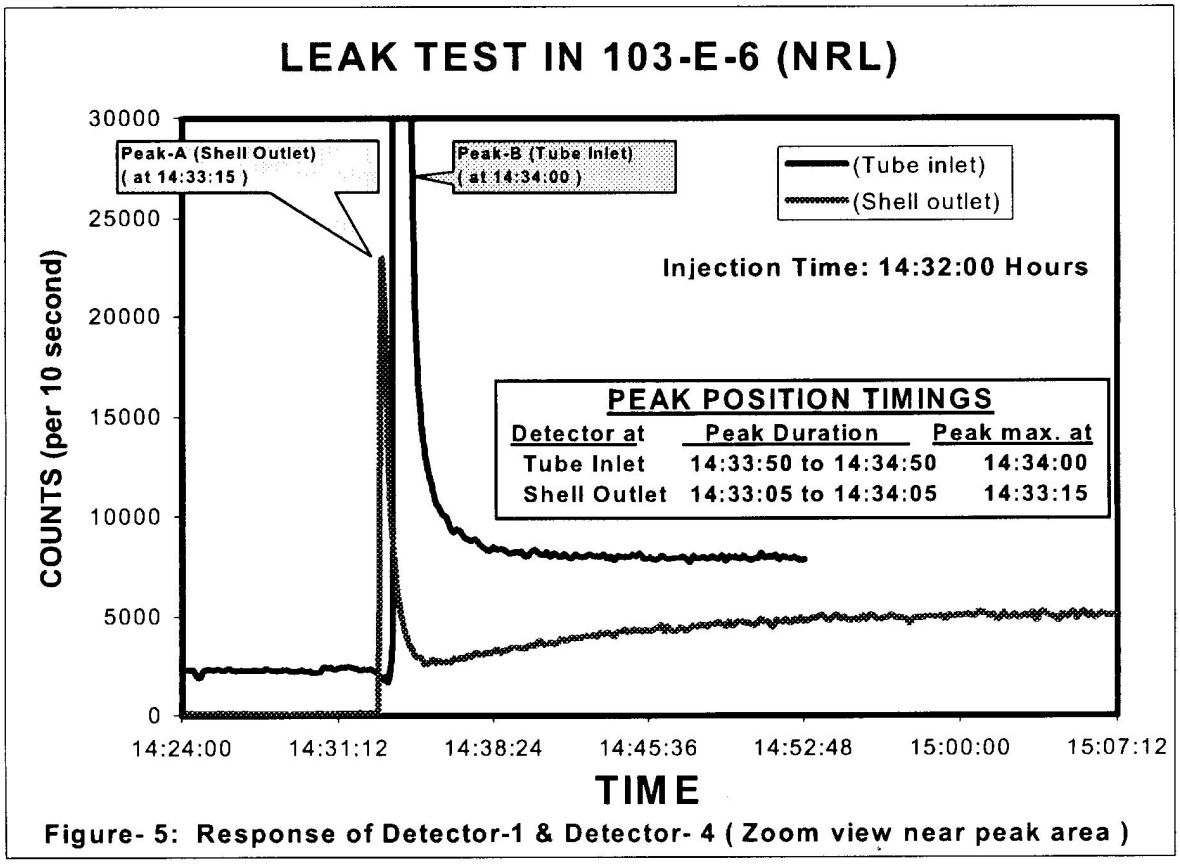

Figure- 5: Response of Detector-1 & Detector- 4 (Zoom view near peak area)

6. DETERMINATION OF RESIDENCE TIME OF MATERIAL IN DIGESTER TUBES NEW FIBER LINE PLANT, PACKAGES, LTD., LAHORE

The objective of the subject experiment was to determine the residence time of material (wheat straw + steam) in Digester Tubes (three tubes in series, with 12 mm thick steel wall) of New Fiber Line (NFL) Plant at Packages Ltd., Lahore. Technetium-99 m (Tc-99 m) radiotracer was used for this purpose. About 7 mili Curi (mCi) of Tc-99 m activity was injected before the inlet of digester tube-1. Radiation detectors were placed at the inlet of digester tube-1, outlet of digester tube-1, outlet of digester tube-2 and outlet of digester tube-3 as shown in figure-1. Scintillation detectors, NaI(Tl), were used to detect the radioactivity of the injected radiotracer.

Computerized data acquisition system was used to acquire data from radiation detectors and display the same on computer screen in real time. The experimental data was further processed & analyzed and the results are shown in figure-2 & figure-3.

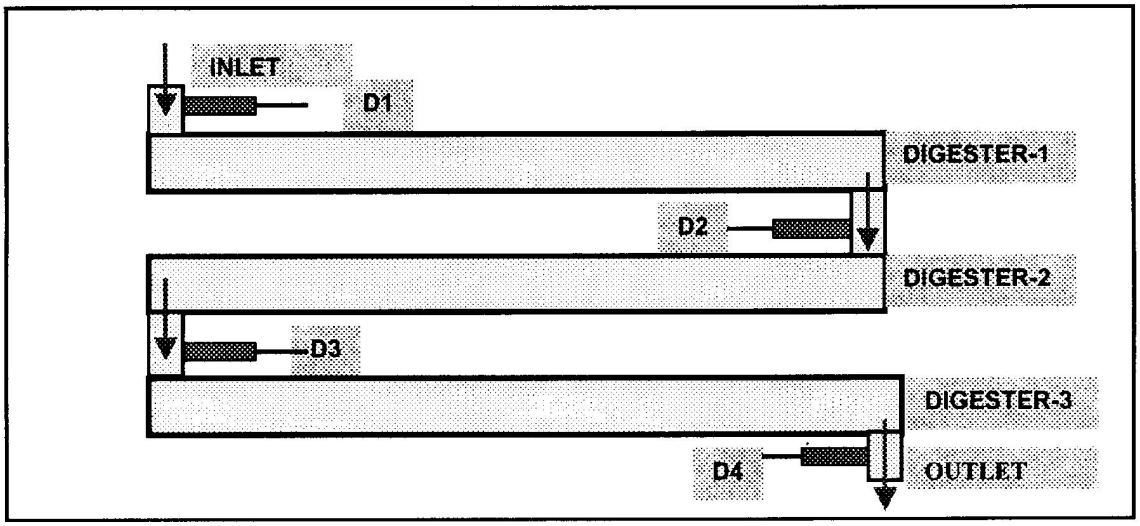

Figure-1: Schematic of NFL Digesters in series and installation of detectors.

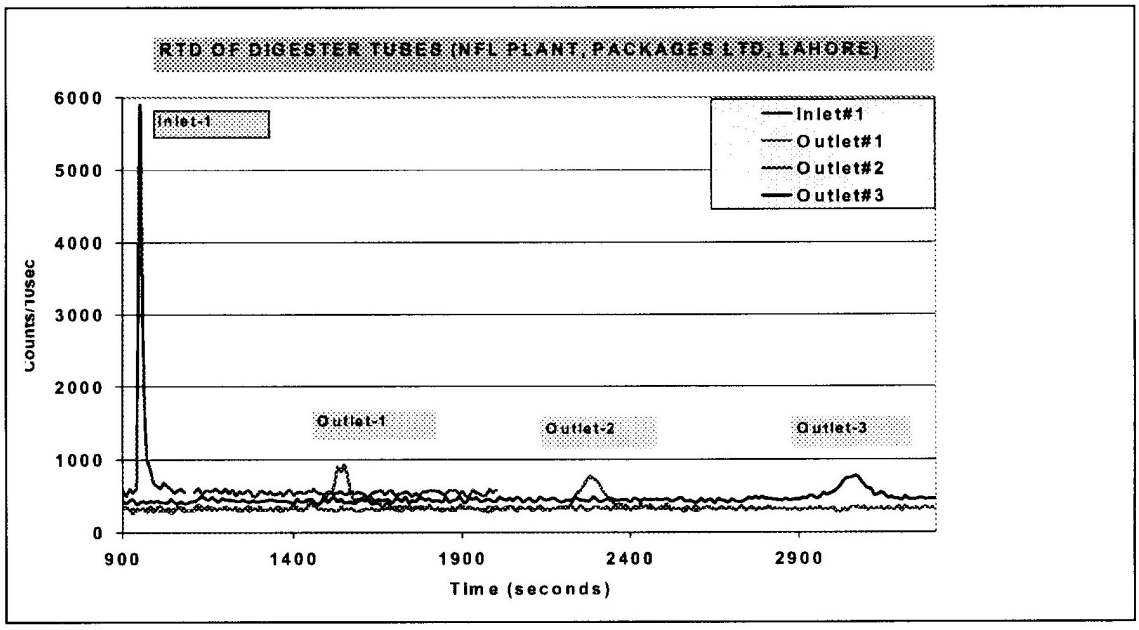

Figure-2: Tracer Response of Radiation Detectors.

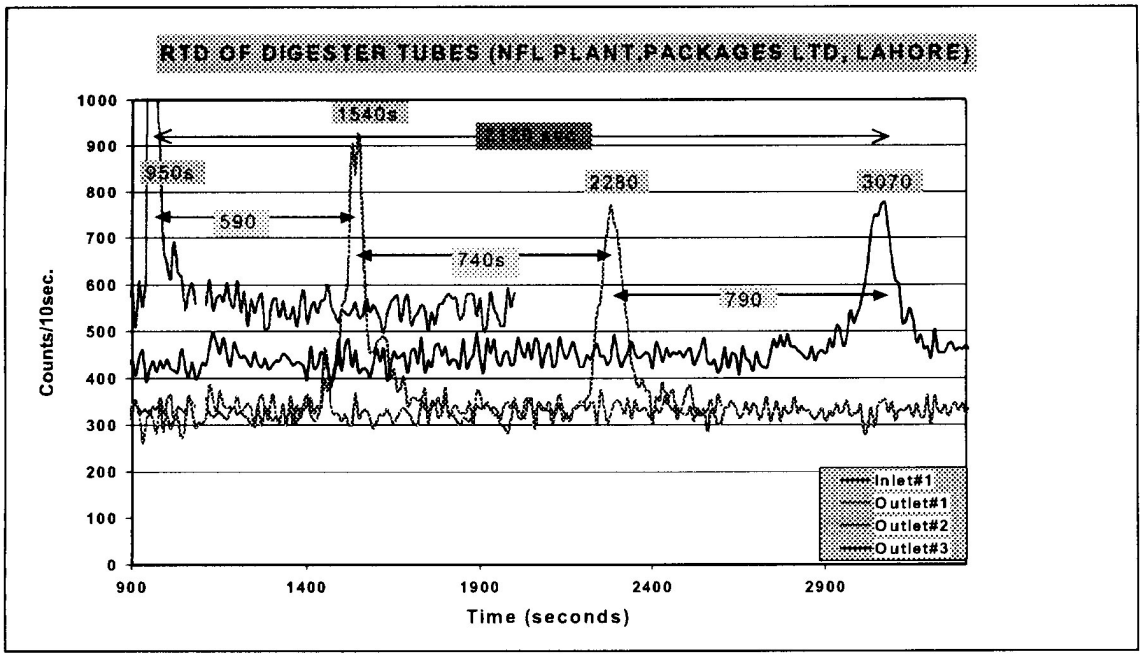

Figure-3: Tracer Response and Residence Time of Material in Digester tubes.

RESULTS/CONCLUSIONS

The analysis of tracer data shows that the material inside the digester is behaving almost like a plug flow. The residence time of material in digester tubes 1, 2 & 3 is 590 seconds, 740 seconds & 790 seconds respectively. The total residence time of material in all three digester tubes is 2120 seconds (35.33 minutes). All radiological safety and protection procedures were followed strictly. The area was monitored after completion of the experiment and was found safe.

7. DETERMINATION OF MIXING TIME OF SIZE AND ALUM IN PULP CHEST AT CENTURY PAPERS & BOARD MILLS, KASUR, PAKISTAN

The objective of the subject experiment was to determine the mixing time of chemicals (SIZE & ALUM) in wood pulp chest at Century Paper and Board Mills Ltd. The total volume of the constituents (wood pulp, OBA, SIZE, STARCH, SSP, STRAW BL. PULP, BROKE PULP, ALUM) of mixing tank is about 35 cubic meters. The constituents are added in the order as mentioned above and are mixed with the help of propeller mixer. Technetium-99 m (Tc-99 m) radiotracer was used for determination of mixing time of SIZE and ALUM in the rest of the material. Radiation detectors [NaI(Tl)] were placed in each corner of the mixing tank at a suitable height from the bottom ensuring that the detectors should not collide with the propeller. Two radiotracer injections were made. For the determination of mixing time of SIZE, about 3 mili Curi activity of Tc-99 m was injected. For the determination of mixing time of ALUM, about 5 mili Curi (mCi) of Tc-99 m activity was used. The tracer was injected in the respective chemical and mixed with it before its introduction into the pulp. Finally, the tracer was injected into the pulp chest, along with the respective chemical, by operating respective valves. Automatic data acquisition system (rate-meters, datalogger, laptop computer) was used to retrieve radiotracer data from the detectors and display the same on computer screen in real time. The experimental data was further processed & analyzed and the results are shown in figure-1 & figure-2 below.

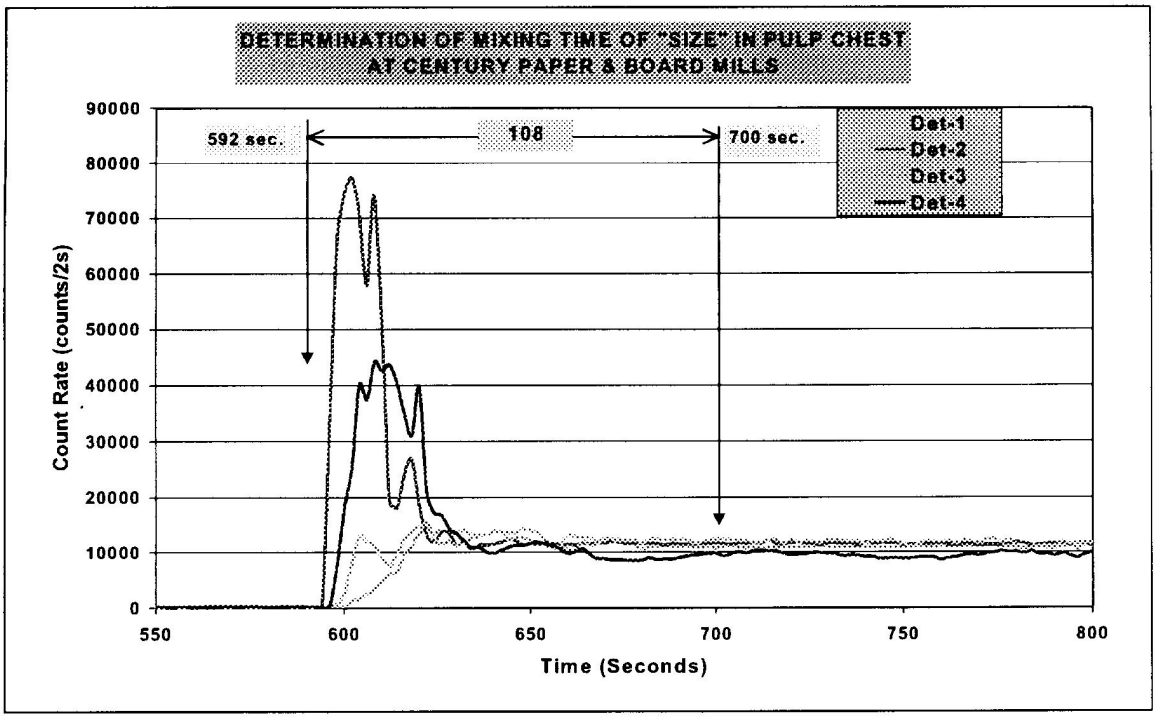

Figure-1: Determination of Mixing Time of SIZE

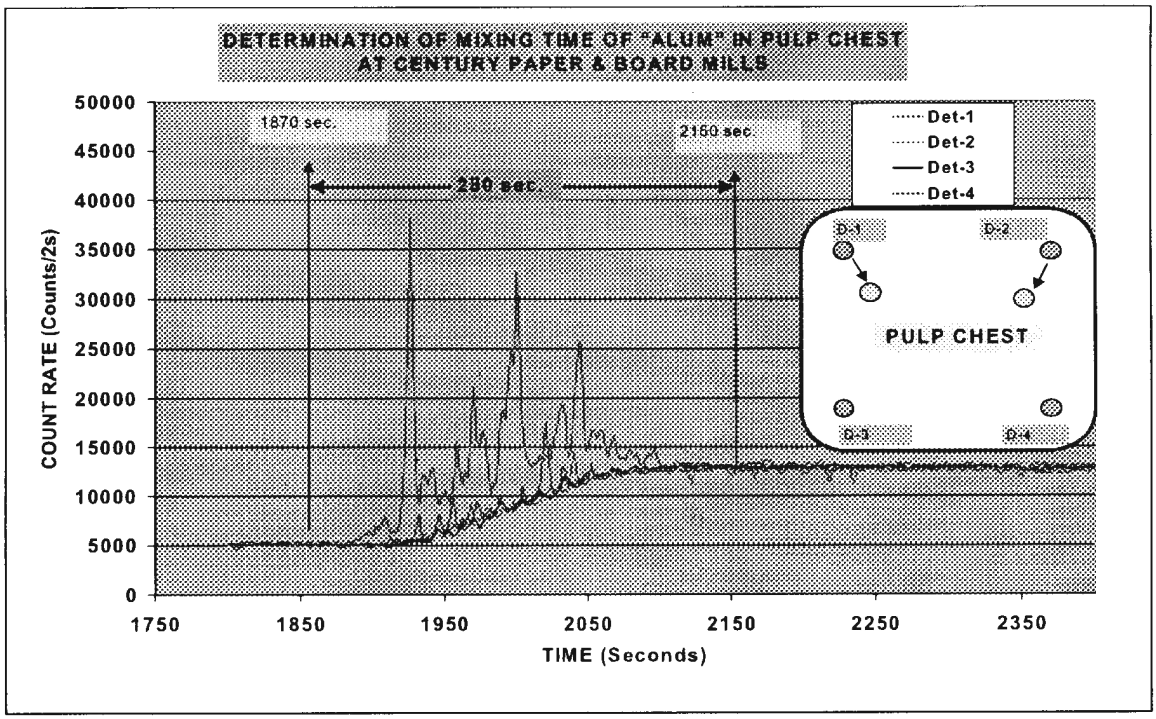

Figure-2: Determination of Mixing Time of ALUM

RESULTS/CONCLUSIONS

The analysis of tracer data shows that the size mixes with the wood pulp in 108 seconds While the ALUM mixes in 280 seconds after it is added into the mixing tank. In routine operation, SIZE is being mixed for 300 seconds while ALUM is being mixed for 1200 seconds. The positions of detector-1 and detector-2 are disturbed after the agitation starts. As a result the detector-1 & 2 move from their original positions (figure-1) to new positions towards the middle of the mixing tank (please see figure-4). However, it does not effect the final result much. The detector-1 has registered highest activity and degree of variation. This is because this detector was placed just near the injection point. It may be mentioned that the mixing time determined by tracer experiment only depicts the mixing of SIZE and ALUM with the rest of the material inside the mixing tank. This is nothing to do with any reaction time and/or coating of the wood pulp with chemicals, etc. If such factors are important for the subsequent process, these may be considered separately. All radiological safety and protection procedures were followed strictly. The area was monitored after completion of the experiment and was found safe.

DISCUSSION

WIDJANG H. SISWORO

1. To respond the global issue on sustainability and self refiance of nuclear Research institute how your institute to plan and to propose annual budget ? Does your institutes mainly depend upond the budget received from the government to run the programme ? Does your institutes seek for or tax financial support from public, Industrial sectors and other institutes ? if yes can you estimate how many percent your institutes annual budget come from public/industrial sectors.
2. Based on your experience which nuclear technique should be developed that will have a greater probability or greater chance the public or industrial sector to run Batan nuclear to get the financial support from programme ?

ISHAK SAJJAD

1. The commercialization of isotopic techniques is different of becomes easy if you have big share of private industry we had some success to earn money from IAEA by analyzing samples from many countries and projects sponsored by private sector. Presently, we are only getting our salaries from Government, the running expenditure is earned by us.
2. Any techniques that would economize the industry expenditure. Radiotracer use in leak detection, coloum scanning, NDT techniques are move probable to earn money for which one has great communication with industry.

SUGIHARTO

1. What benefits advantages can be obtained from the application of TLA technique ?
2. To what extend the TLA techniques have been applied in Pakistan ?

ISHAK SAJJAD

1. TLA can be used to study wear/tear in engines, carrision studies in pipelines etc.
2. A. For carrision studies in pipeline – statistik 2002
   B. For wear/tears in Piston rings – first starter