RADIOISOTOPE APPLICATIONS ON FLUIDIZED CATALYTIC CRACKING UNITS

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SUMMARY.

Radioisotope techniques utilizing both radioactive tracers and sealed sources of radiation are being used increasingly as diagnostic tools for process optimization and trouble-shooting on Fluidized Catalytic Cracking Units in oil refineries. These studies are among the most challenging in the field of industrial radioisotope applications. Case studies are presented to illustrate the usefulness of the technology in obtaining information about the fluid dynamics, mass transfer properties and material distribution inside full scale operating units. This information is difficult or impossible to obtain by any other means and is of great relevance to the refinery operator because of the economic importance of the units. Technological trends and potential developments are also discussed.

1. INTRODUCTION

The Fluid Catalytic Cracking Unit (FCC) is arguably the economic heart of an oil refinery and is used widely to upgrade relatively low value heavy oils to gasoline and other light hydrocarbons. The optimal performance of the FCC is vitally important to successful refinery operations since relatively small improvements in unit efficiency can lead to substantial increases in revenue, resulting from increased gasoline yield.

From an operational point of view, FCCs are notoriously difficult. Even though the technology has been in use for many years and in spite of the fact that hundreds of units are installed world-wide, inefficiencies and malfunctions are, nevertheless, commonly encountered. This results directly from the inherent complexity of the process. The reaction section of an FCC is a dynamic system in which vaporised high-molecular weight hydrocarbon chains are fractured in the presence of a solid catalyst, carried in a high-velocity flow of steam (1). The vapour residence time in the reaction section of the unit is usually significantly less than 10 seconds. Because of the arduous process conditions, the units are of heavy construction and this, together with the abrasive properties of the fast-moving catalyst makes it very difficult to study mass transfer and fluid dynamics using invasive instrumentation.

The most effective way to obtain information about the operation of the FCC is to utilize radioisotope technology. Radioisotope methods are particularly suitable because of their sensitivity, which allows flow patterns within the large-scale units to be traced successfully, and because of their unique ability to effectively visualise the distribution of materials within the operating plant.

This was first recognised over 40 years ago when radioactive tracers were used to study catalyst flows inside fluid catalytic systems (2,3).

Since then, the technology has been continuously refined (4,5,6) so that, at the present time, radioisotopes are used extensively to trace catalyst, vapour and steam flows.

Radioisotopes as sealed sources of gamma-radiation have long been used to locate catalyst levels inside the process vessels and to measure catalyst density distributions 7,8). These methods, and variants of them are still in use today (6).

This paper presents a number of case studies as examples of the many ways in which radioisotope techniques are used to study FCCUs and identifies developments in the technology which hold promise for the future.

2. RADIOACTIVE TRACER STUDIES

2.1 Principles

The movement and distribution of all of the process streams in the unit - catalyst, vapour and steam - can be traced individually using radioisotope labelling. Radioactive material in an appropriate form is injected as a sharp pulse into the process stream of interest. In this way, a representative portion of the flowing stream is "tagged" with radioactivity and its subsequent movement through the unit can then be followed using radiation detectors strategically located on the vessels and pipework.

The volume of the injected material is small so that the process is not perturbed. Additionally, because of the high detection sensitivity the activities injected are relatively small so that there is no measurable hazard to plant personnel. Access to the unit need only be restricted for the duration of the injection so that operations are not disrupted to any significant extent.

2.2 Methodology

2.2.1 Scope

Radioisotope technology has been applied successfully to study all parts of the FCC. So wide has been the range of applications that a comprehensive survey is impossible in the space allotted to this paper. Instead, attention is focused on studies of the reactor/riser and stripper sections as being illustrative of the range of possible applications.

2.2.2 Radiotracers

The vaporised feed and steam flows are almost always traced using one of the gaseous radioisotope ^{41}Ar, ^{85}Kr or ^{79}Kr.

The catalyst is reliably traced by taking a sample of catalyst from the unit and irradiating it in a nuclear reactor to produce the radioisotopes ^{140}La and/or ^{24}Na. The attraction of this approach is that the catalyst is its own tracer and this facilitates detailed study of its behaviour in the FCC environment. For example, the dynamics of different particle size fractions can be investigated.

An alternative to catalyst irradiation which may be useful in certain applications is the technique of "in-situ labelling". This involves the injection into the catalyst stream of an aqueous solution of a radioactive salt (for example $^{24}Na_2CO_3$). Once inside the unit, there is a rapid evaporation of the water and the $^{24}Na^+$ ion attaches itself to the catalyst thereby producing a pulse of labelled material.

2.2.3 Field Measurements: Equipment Arrangement

To follow the movement of the radiotracer through the FCC, sensitive radiation detectors are positioned at appropriate locations on the unit. The precise deployment obviously varies from one application to another but a typical arrangement for studies on the reactor, riser and stripper is shown in Figure 1.

Tracer is injected into the system using backing pressure from a nitrogen cylinder. The response of the detectors to the passage of the tracer pulse is recorded as a function of time on a data-logging system.

The general principles of measurement may be illustrated with reference to a simple example. Suppose that it is desired to study the movement of catalyst up the riser. The radio labelled catalyst is injected as a pulse at the base of the riser (Figure 1). By studying the responses and time-sequencing of detectors D_1-D_4 (Figure 2) the velocity of the catalyst through different sections of the riser can be measured and from this information the catalyst acceleration can be calculated.

By carrying out similar measurements using a pulse injection of gaseous radiotracer it is possible to measure the vapour velocity. Comparison of the results of the two measurements permits the vapour/catalyst slip velocity to be calculated. This is an important parameter since it influences the contact time of vapour and catalyst which in turn influences the cracking pattern of the hydrocarbon chains.

Analysis of the shapes of the detector response curves provides information about the mixing and dispersion characteristics of the flow up the riser. For example, by computing Inverse Peclet Numbers, deviations from perfect plug-flow can be quantified. Should changes subsequently be made to the riser to improve the dispersion characteristics, the measurements can be repeated to check the effectiveness of the modifications.

2.3 Case Studies

The following case studies relate to an FCC which was operating at reduced efficiency. Catalyst circulation was impaired and additionally, catalyst powder was appearing in the gaseous product stream. Radiotracers were used to investigate the cause of the problems.

2.3.1 Flow Maldistribution in the Stripper

This was investigated by injecting a pulse of irradiated catalyst into the base of the riser and examining the responses of detectors D14-D17, placed around the stripper at N, S, E and W locations. The response curves are shown in Figure 3. The asymmetry of the response curves is apparent and is indicative of excessive catalyst flow down the South quadrant. To investigate the reason for this flow maldistribution, the flow of stripping steam was investigated using a ^{85}Kr tracer. This was injected as a pulse into the stripping steam ring (Figure 1) and the responses of Detectors D14-D17 were compared (Figure 4). Again, flow maldistribution is apparent, but in this case there is a disproportionate amount of steam going up the North side of the Stripper.

From this evidence it was deduced that the steam ring was the source of the problem : the large upflow of steam in the North quadrant impedes the downflow of catalyst and gives rise to excessive catalyst traffic down the South quadrant - hence the catalyst circulation problem.

2.3.2 Investigation of the Operation of the Riser Termination Device

The purpose of the Riser Termination Device (RTD) is to direct the catalyst downwards into the Stripper and the reaction products into the overhead vapour line. In reality, complete disengagement is almost impossible to achieve and for this reason the vapour passes through cyclones, the function of which is to remove residual catalyst before exiting the vessel. (Figure 1).

In the case in question, in spite of the presence of the cyclones, catalyst dust was exiting in the vapour stream. The problem was investigated by injecting irradiated catalyst into the base of the riser.

The response curves of detectors D8 and D9, located in the upper part of the reactor (Figure 1) are well-defined and contain at least two components (Figure 5). From the time of arrival of tracer at the detectors, together with the sharpness of the response curves it is clear that a significant fraction of the catalyst is passing directly up the vessel. The response of detector D10 (Figure 6) located on the overhead line provides confirmation of catalyst carryover.

It was deduced from these results that either the termination device was of inefficient design or it was damaged. At shutdown, visual inspection confirmed that the device had become partially dislodged.

The above examples are illustrative of how on-line inspection can provide important information about the condition of the unit. On the strength of this information, maintenance and design engineers were alerted to potential problems with the steam-ring and with the riser termination device and were able to plan modifications prior to shutdown. The steam ring was realigned and the termination device was replaced by another of completely different design.

Radiotracer tests subsequently carried out after start-up showed that the objectives of the modifications had been achieved.

3. SEALED SOURCE TECHNIQUES

Gamma-ray transmission is the most commonly used technique for the investigation of FCC performance. If a beam of gamma-rays of intensity I_0 impinges on a material of thickness x and density d, then the transmitted radiation, I, is given by:

$$I = I_0 \exp - \mu dx \quad (1)$$

where μ is a constant known as the mass absorption coefficient. Therefore, if a radioactive source is positioned on one side of a medium and a radiation detector on the other such that their separation, x, is kept constant, the density of the intervening material may be inferred from measurements of the transmitted radiation. This principle may be applied in a number of ways - for example, to investigate density variations over time as the catalyst circulates, to measure catalyst levels in the Stripper or to determine the mean density of catalyst across a pipe diameter.

To provide information about the spatial distribution of catalyst in the cross-section of a vessel, a technique known as "Matrix Point Mapping" is used. The principle is illustrated in Figure 7. This technique is useful in determining relative density distributions. For absolute measurements it is desirable to conduct equipment calibrations on similar pipework. Ideally, a blank scan would be performed on the actual piping when out of service.

4. TRENDS AND DEVELOPMENTS

4.1 Data Collection

The most obvious trend is in the use of increasing number of detectors for radioactive tracer studies. It is now common for 20-30 detectors to be deployed in an FCC study. this reflects the plant engineers' requirements for more detailed information about the operations of the process. The trend is expected to continue as process models became more sophisticated.

4.2 Novel Tracers

It is anticipated that radioisotope generators will be used more and more for catalyst labelling. The $^{113}Sn/^{113m}In$ system has already been used successfully for this purpose but other generators, such as $^{68}Ge/^{68}Ga$ are being investigated.

ANSTO fullerines (9) offer interesting possibilities as carriers for gaseous radiotracers. Noble gases can be incorporated within the C_{60} structure of the fullerine. Neutron irradiation results in a system which contains a high volume density of the activation product. thus, enhanced activities of isotopes such as ^{41}Ar or ^{79}Kr may be transported to the work-place, thereby alleviating problems associated with using these isotopes at sites which are geographically remote from a nuclear reactor.

4.3 Industrial Gamma-Ray Tomography

It is clear that the use of a tomographic system would greatly improve the definition of the catalyst density distributions obtained from matrix point mapping (Section 3). This is dependant primarily on the development of a system sufficiently rugged to operate in (often) harsh industrial environments and with sufficient flexibility to be adaptable for use on pipes and vessels within a wide size-range.

4.4 Data Interpretation

The interpretation of detector response curves is often complicated by the fact that the curves may be composed of several overlapping peaks. this results from the fact that the process time constants are comparable with the width of the tracer peaks. The situation is undersirable, since peak-overlap may conceal important information.

Recently, excellent work on response-curve decomposition has been reported (10). Application of this technology will increase both the quality and the quantity of the information obtained from tracer studies.

The results of radioisotope studies have already proved to be of great value in developing and validating mathematical models of FCC units. These applications will become even more important as the sophistication of the models increases.

5. CONCLUSIONS

Radioisotope technology is a powerful tool for the investigation of many aspects of the performance of FCCs. The information obtained about the fluid dynamics of the process streams, mass transfer properties and material density distributions is often crucial to the understanding of process operations and leads to significant economic benefits in terms of optimization and trouble shooting. Generally, it is impossible to obtain this information in any other way.

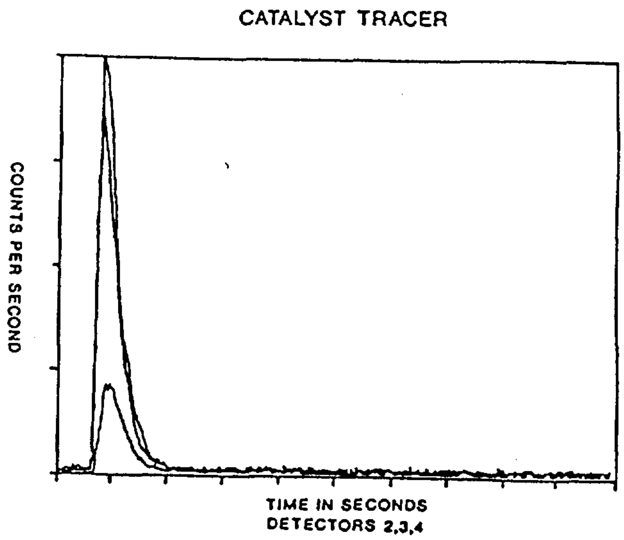

FIGURE 2. Flow up the riser. Detector Responses

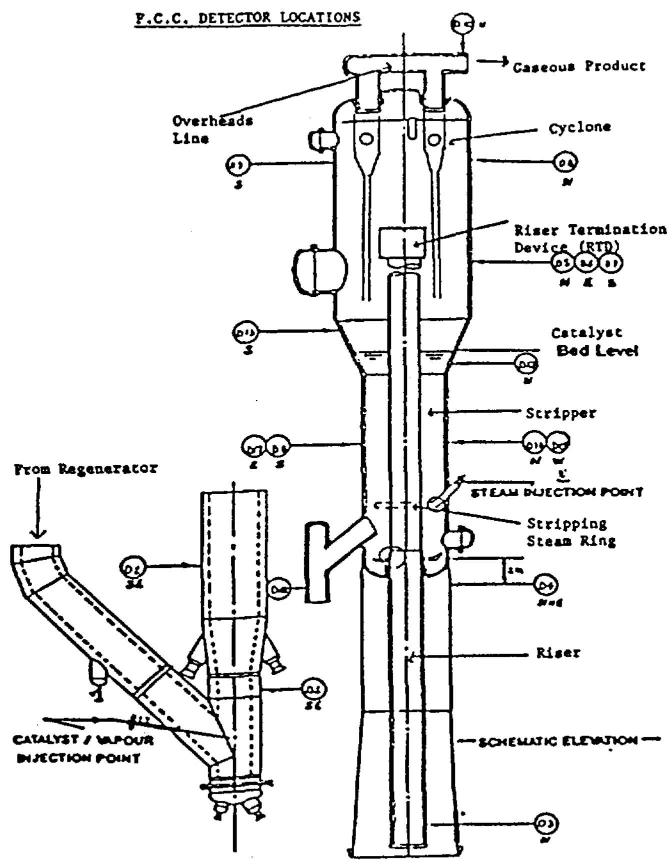

FIGURE 1. Equipment Layout for Radioactive Tracer Studies.

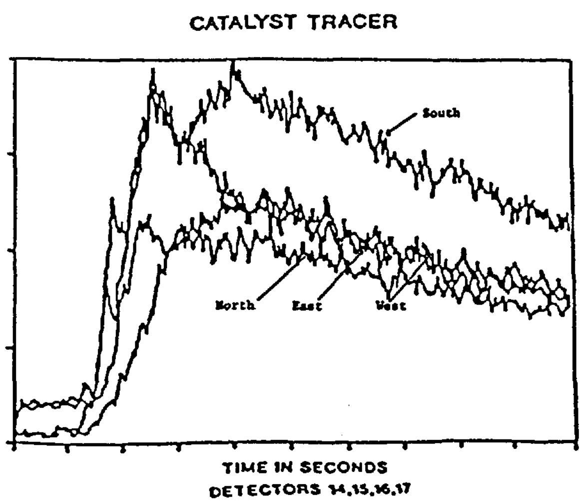

FIGURE 3. Catalyst Flow Down Stripper. Detector Response Curves

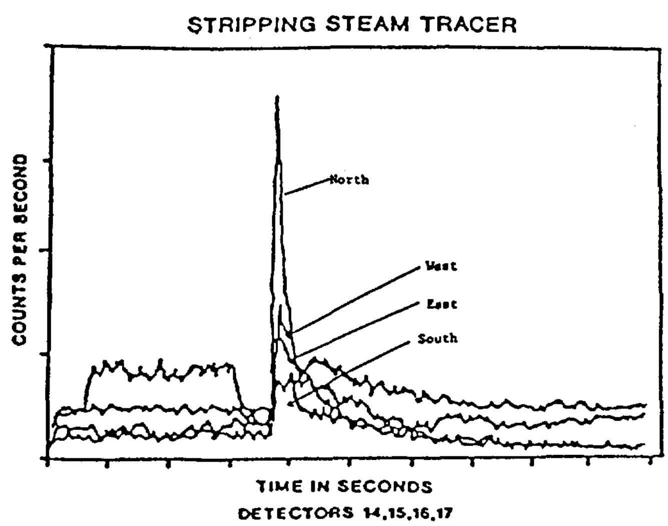

FIGURE 4. Steam Flow up the Stripper. Detector Response Curves

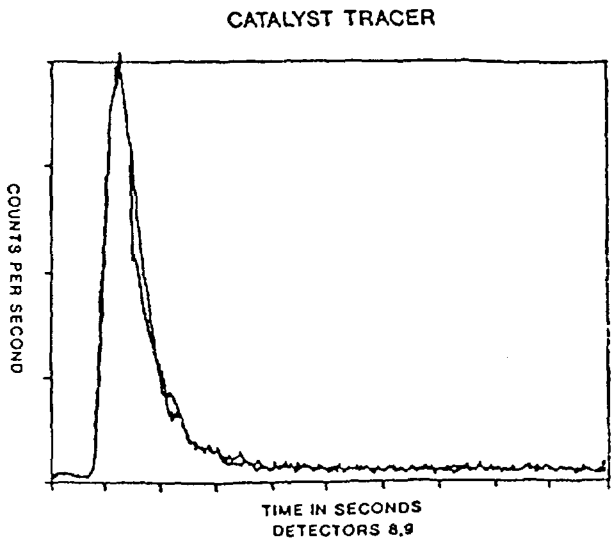

FIGURE 5. Investigation of Riser Termination.
Response of detectors on the Reactor.

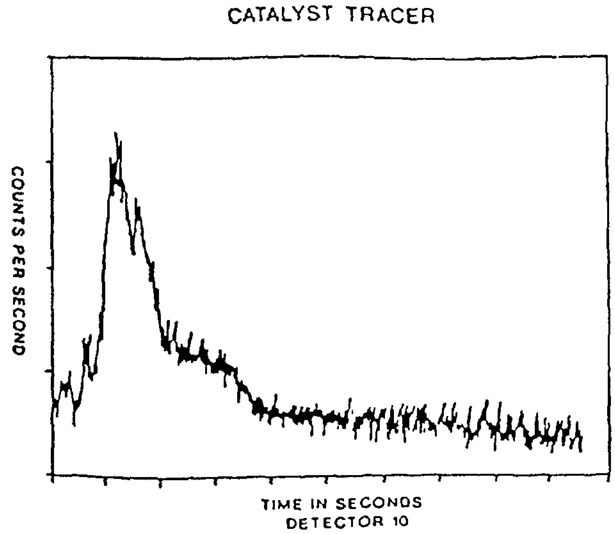

FIGURE 6. Investigation of Riser Termination.
Response of Detector on Overhead Line.

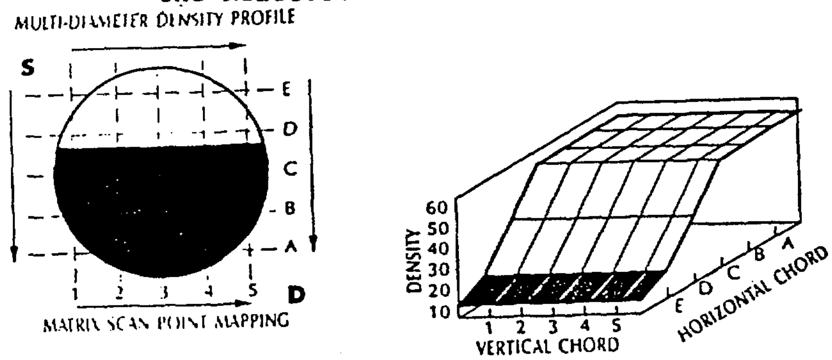

FIGURE 7. Sealed Source Techniques for Catalyst Density Studies.

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