Study on the Evaluation of the Remnant Catalyst in the Desulfurization Reactor by Analyzing γ-Spectrum

Jong-Kyu Jeon, Sung-Hee Jung, Jong-Bum Kim, Jin-Seop Kim
Korea Atomic Energy Research Institute, P.O. Box 105, Yuseong, Daejeon, Korea, 305-353, jkjeon@kaeri.re.kr

1. Introduction

Desulfurization of petroleum feedstocks is an important process with wide reaching implications for the petroleum industry and the environment [1]. At this point of view, the diagnosis of desulfurizing process gives significant information to judge the optimal time to replace the spent catalyst by recognizing the efficiency and the amount used catalyst of the process. The evaluation of the catalyst lifetime in a desulfurizing process in a petrochemical plant has been carried out by chemical analysis of the specimen taken from the specific regions. However, it has a drawback that the estimation of the precise reaction zone is difficult and a number of gathering points for specimen are necessary. In addition, it is difficult to evaluate catalyst lifetime during the operation of the process because the collection of specimen is available after the shutdown of process. In order to evaluate its lifetime of on-line process, the introduction of application technology for the diagnosis of industrial process using gamma radiation was considered and a new measurement for the evaluation of reaction zone and density variation of catalyst in a desulfurizing vessel using scattered gamma radiation has been studied. Vertical density profile of packed materials in the reactor at various elevations can be plotted by detecting and analyzing scattered radiation, which shows different counts depending on the density of materials when traversing the reactor [2, 3]. The reaction zone between unused and used catalyst and relative amount of two materials can be evaluated by analysis of minute difference of scattered gamma radiation spectra at a specific energy region.

2. Experimental

The gamma radiation source used in the field was ^{60}Co (210mCi, KAERI) sealed in the stainless steel capsule and collimated in the sealed source holder made of lead. The desulfurizing vessel (height 18.4m, diameter 2.65m) consists of Cobalt-Molybdenum catalyst ($CoMo_x$), upper Zinc oxide (ZnO), and lower Zinc oxide (ZnO) catalyst layers. The upper ZnO catalyst layer was replaced in 2002, and the lower ZnO layer is the additional catalyst layer to prevent the outflow of sulfur to the downstream process due to the lifetime of upper ZnO layer. The calculation of the optimal time of replacement plays an important role in maintenance of product quality and an enhancement of process efficiency as well as cost saving.

The measurement of the gamma radiation was performed for 1 minute per each point at intervals of 10cm for the scan range from the lower part of $CoMo_x$ layer to the hollow region above the lower part of ZnO layer. A 2 inch NaI(Tl) scintillation detector(Model 802, Canberra), a NIM (Nuclear Instrumentation Module, Canberra) equipped with spectroscopy amplifier (Model 2022, Canberra), PM tube base/preamp (Model 2007P, Canberra), and HV power supply (Model 3102D, Canberra), and a portable multi-channel analyzer (MCA-8000, Amptek) were used for the measurement of gamma radiation.

3. Result and Discussions

Fig. 1 displays the range and orientation of measurement, and the vertical profile of gross counting values calculated from the gamma radiation spectra.

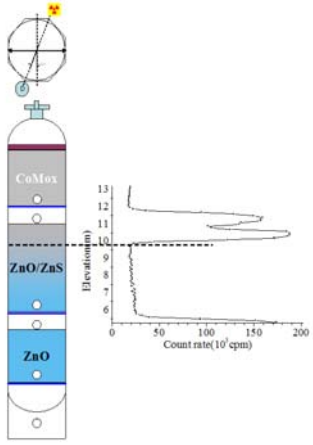
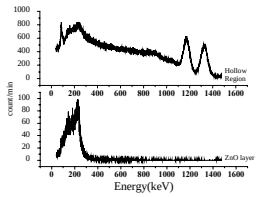


Fig.1 Vertical density profile of desulfurizing vessel by gross-counting method

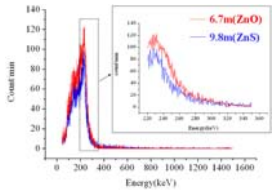
Each region shows the difference of the intensities of transmitted or scattered gamma radiation catalyst layers and hollow region in the vessel. Low gross counting values at the upper region result in the lower part of the $CoMo_x$ layer located in the upper region of the desulfurizing vessel. The hollow region between $CoMo_x$ layer and the upper ZnO layer was confirmed at the section between 9.9m and 11.9m. Low gross counting values at the section between 5.7m and 9.9m mean the scattered gamma radiation through the ZnO/ZnS layer, and the section between 5.3m and 5.7m shows the hollow region between the upper ZnO/ZnS layer and the lower ZnO layer. The height of the upper ZnO/ZnS layer during the process operation was verified as 4.2m from the results of the vertical profile. This is 1.3m lower than the height value in the vessel drawing and it reveals that the measurement was precisely performed by confirmation from the process

operator that the actual height of the ZnO layer after the replacement in 2002 was 4.3m.

Fig. 2(a) displays the comparison of the measured gamma radiation spectra through the hollow region and the desulfurizing catalyst layer. The scattered spectrum at the low energy region was only detected at the desulfurizing catalyst layer whereas the spectrum of the hollow region detected shows the typical peaks of ^{60}Co gamma radiations and scattered gamma spectrum along the entire energy region. It can be due to the scattering and shielding effects by the thick catalyst packed with high pressure in the vessel with a large diameter (2.7m)[3]. Two scattered gamma radiation spectra at 6.7m and 9.8m, which are assumed as the typical region of ZnO and ZnS, respectively, are displayed in Fig 2(b) to confirm the chemical variation of catalyst packed in the desulfurizing vessel from the comparison of scattered gamma radiation spectra of ZnO/ZnS layer at two different scanning points. The difference of intensities at the energy region between 230 and 270keV was found even if there is no significant difference between two spectra in the entire energy region. Therefore, the sums of counts corresponding to the height at this energy region for each scanning point of ZnO/ZnS catalyst layer were displayed in Fig. 3 in order to differentiate ZnO from ZnS catalyst layer.



(a)



(b)

Fig. 2 (a) Comparison of scattered gamma spectra at empty and ZnO packed region, (b) Comparison of scattered gamma spectra at 9.8m (ZnS) and 6.7m (ZnO) in the reactor

Based on the sums of counts at the low energy region measured in the middle section between 7.4m and 9.0m (1.6m), the upper section between 9.0m and 9.9m (0.9m) and the lower section between 5.7m and 7.4m (1.7m) show lower distribution area and the higher one, respectively. It means that ZnS has lower count values than the count value of ZnO due to the change of bulk density from 1.17g· cm^{-3} to 1.35g· cm^{-3} when unused catalyst ZnO reacts with hydrogen sulfide (H_2S) and produces ZnS[3, 4]. Therefore, it means that the majority of catalyst in the upper section with low count values(0.9m) was transformed as ZnS. the lower section of reactor, which shows high count values, is the region of ZnO which is mostly unreacted with hydrogen sulfide, and the reaction zone of desulfurization was in the range between 7.4m and 9.0m (1.6m).

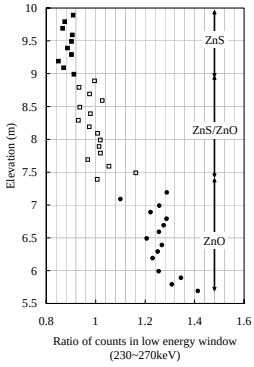


Fig. 3 Variation of relative count ratio in low energy window at various elevations

4. Conclusion

It was revealed that scattered gamma radiation can be used to evaluate relative amount of remaining catalyst in the desulfurizing process. The exact height of packed catalyst was calculated by the analysis of vertical density profile from gamma scan by gross-counting method. In addition, scattered gamma spectra in the low energy window displayed the reaction zone and level of used and unused catalyst in the reactor.

It is proven that applicability of this diagnosing method to other packed bed reactors having density variations.

ACKNOWLEDGEMENT

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REFERENCES

[1] J. Dvorak, T. Jirsak, J.A. Rodrigurz, Fundamental studies of desulfurization processes: reaction of methanethiol on ZnO and Cs/ZnO, Surface Science, Vol. 479, p. 155-168, 2001

[2] J.S. Charlton, Radioisotope techniques for problem solving in industrial process plants, Leonard Hill, Glasgow and London, pp.214-217, 1986

[3] G.A. Johansen, P. Jackson, Radioisotope gauges for industrial process measurements, John Wiley & Sons, pp.213-231, 2004

[4] N. Tsoulfanidis, Measurement and detection of radiation, Hemisphere Publishing Corp., pp.141-155, 1983