

## Properties Analysis of Spent Catalyst for Fixed-Bed Residue Hydrotreating Unit: Radial Distribution of Deposited Elements in Spent Catalyst Particles

SUN Yudong<sup>[a],\*</sup>; YANG Chaohe<sup>[a]</sup>; LIU Ziyuan<sup>[a]</sup>

<sup>[a]</sup> College of Chemical Engineering, China University of Petroleum, Qingdao, China.

\*Corresponding author.

**Supported by** “The Fundamental Research Funds for the Central Universities (Grant No. 27R1104049A)” and “PetroChina Innovation Foundation (Grant No. 2011D-5006-0405).”

Received 16 August 2012; accepted 9 November 2012

### Abstract

14 spent catalysts, which were sampled from a commercial residue hydrotreating unit at the end of an operation cycle, were analyzed by SEM to describe elements distributions along the radial direction of particles. Different from laboratory equipment, on the whole, V, Ni and S showed U-shaped pattern along the radial direction of spent catalysts. The catalyst bed has been penetrated by deposited metals and deposited massive metals on catalyst, so the pore size of catalyst decreased, diffusion resistance increased and reactants entered internal of the catalysts more difficultly. Most of the organometallic compounds hydrotreated and deposited on outside of the catalyst particles. It is showed that metals deposited on catalyst in forms of metal sulfides because the points of high metal content also have high sulfur contents unexceptionally. The structure of high metal deposition catalyst was destroyed obviously or massive irregular material has deposited on the external surface. It is verified by SEM that there is no any distribution law for deposited elements along the bed height. The change laws of deposited elements along the bed height and radial direction of particles were influenced by various factors in commercial residue hydrotrating.

**Key words:** Residue hydrotreating unit; Spent catalyst; SEM

Sun Y.D., Yang, C.H., & Liu, Z.Y. (2012). Properties Analysis of Spent Catalyst for Fixed-Bed Residue Hydrotreating Unit:Radial Distribution of Deposited Elements in Spent Catalyst Particles. *Energy Science and Technology*, 4(2), 20-24. Available from: URL: <http://www.cscanada.net/index.php/est/article/view/j.est.1923847920120402.512> DOI: <http://dx.doi.org/10.3968/j.est.1923847920120402.512>

### INTRODUCTION

As the reaction carried through in residue hydrotreating, heteroatom was removed gradually. Besides partial of the S and N element were away from the reactor in forms of H<sub>2</sub>S and NH<sub>3</sub>, all the metal heteroatom and other S, N were deposited on catalyst. The deposition amounts and distributions of various elements on catalyst radial direction are different because the reaction rates of various compounds are different. It has been reported (Tamn *et al.*, 1981; Callejas *et al.*, 2001) that V has smaller distribution parameter ( $\theta_m$ ) and inclines to deposit on the entrance of catalyst pore, but Ni has large  $\theta_m$  and inclines to deposit in inner of the catalyst. The  $\theta_m$  of V increased and Ni decreased during reaction, so the distribution of V and Ni on catalyst changed with the increase of reaction time.

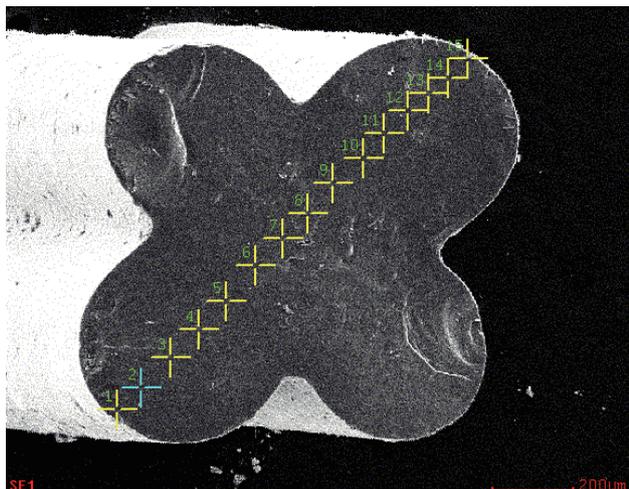
The influences of deposited coke and metals on configuration deactivation are various because deposition positions of coke and metals on catalyst are different. It is an important method to study the deactivation reasons of residue hydrotreating catalyst by researching deposition state and distribution of coke and metals on catalyst. It has great significance for residue hydrotreating catalyst development and pore structure design of support.

### 1. ANALYSIS METHOD

Sediments distribution along the radial direction of commercial spent catalyst was analyzed by SEM. SEM analysis were measured by S-4800 CFE SEM with X-ray Energy Dispersive Spectroscopy (EDS) manufactured by HITACHI Company. The SEM equip with super E×B× detector to enhance image and provide high-resolution electron optics image. The attached EDS can provide high-resolution superficial micro-morphology, meanwhile, quantitatively and qualitatively analyze micro-area composition and element distribution of the sample.

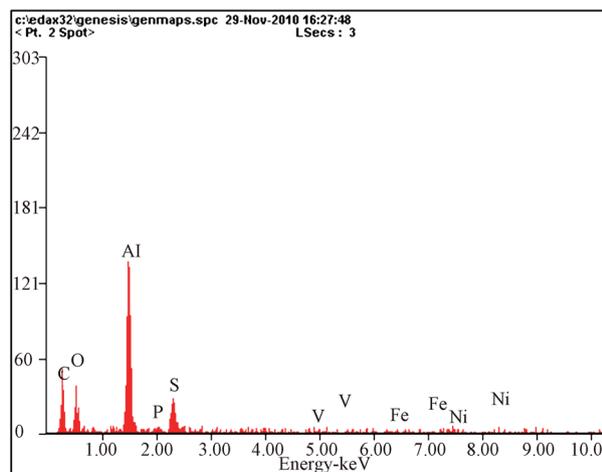
Several catalyst particles, which were sampled from commercial fixed-bed residue hydrotreating unit (Sun,

2011; Sun, *et al.*, 2012) and treated by extraction and drying, were cut along the radial direction. The element compositions on different radial positions of the cutting profiles were qualitatively and quantitatively analyzed by the attached EDS. 15 sites were selected (see Figure 1) to analyze element composition on each profile in order to obtain detailed radial distribution law of deposited elements on catalyst.



**Figure 1**  
**SEM Profile of Residue Hydrotreating Catalyst**

Output results of SEM-EDS analysis are shown as Figure 2. Analysis report of qualitative and quantitative analysis of one site on profile by SEM-EDS is given in Table 1.



**Figure 2**  
**SEM-EDS Analysis Result Map**

**Table 1**  
**SEM-EDS Analysis Result Report Form**

Element	Wt%	At%
CK	54.16	67.38
OK	20.47	19.12
AlK	20.08	11.12
PK	00.63	00.30
SK	04.21	01.96
VK	00.00	00.00
FeK	00.00	00.00
NiK	00.46	00.12
Matrix	Correction	ZAF

## 2. ANALYSIS RESULTS OF SEM

### 2.1 Data Processing

Two catalyst particles of the same sample were analyzed by the above method which came from 14 spent catalyst sample (Sun, 2011) respectively. The original analysis data of SEM show that various deposited elements have not any distribution law along the radial direction of catalyst. It has been found that catalyst particle should be fixed by carbonaceous conductive gel in order to make catalyst particle stable. The carbonaceous conductive gel, especially when gel smear unevenly, can influence carbon distribution and content on catalyst profile. Therefore, the distributions and contents of other elements would also change.

In order to exactly describe elements distribution along the radial direction of catalyst, an invariable referent must be determined to reflect changes of elements content correspondingly. The support of this series catalyst is  $Al_2O_3$ . Al is well distributed along the radial direction of catalyst and its absolute content is constant in a fixed-size area. Al content has no obvious change by Al deposited on catalyst in residue hydrotreating because the content of Al in residue is negligibly small. So, Al content of the test points on profile was used as the evaluation reference and the ratios of other elements content to Al content were adopted as the analysis data. An example of treated analysis result is shown in Table 2.

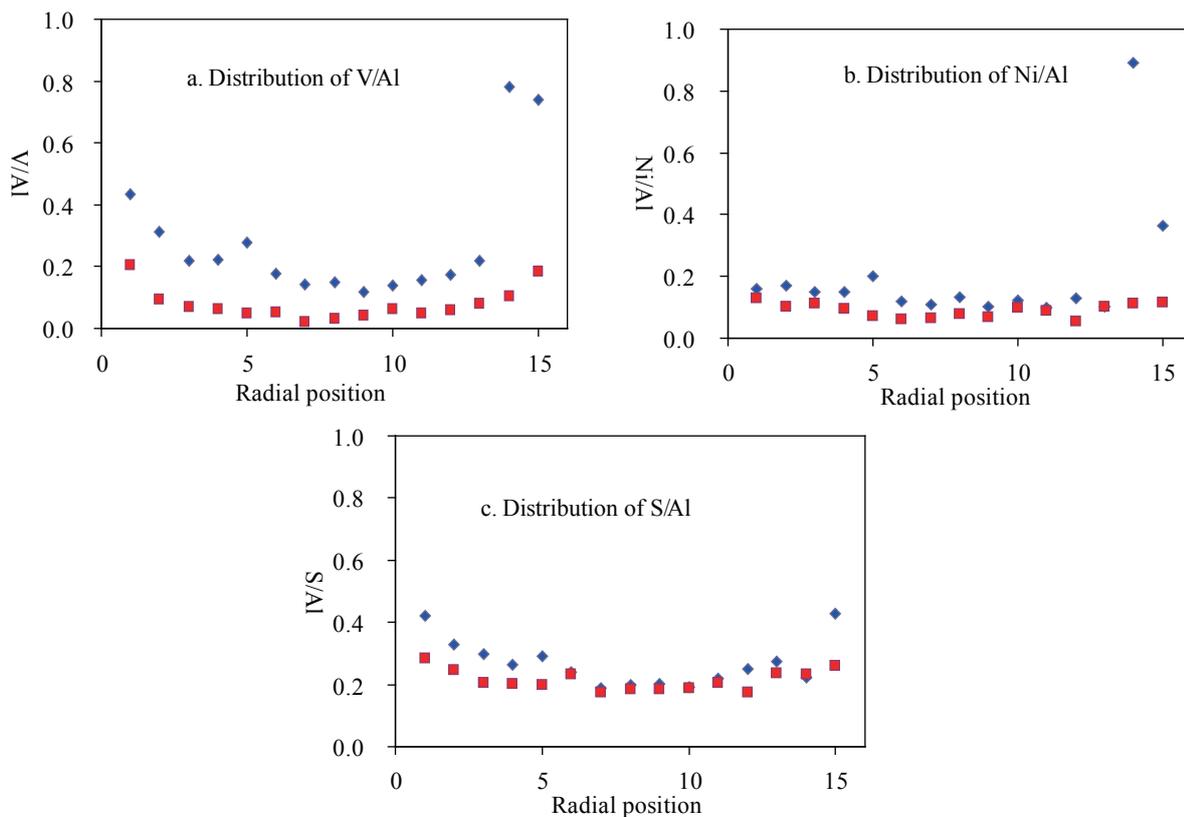
**Table 2**  
**SEM-EDS Analysis Results of 9<sup>#</sup> Catalyst**

Samples elements	1			2		
	S/Al	V/Al	Ni/Al	S/Al	V/Al	Ni/Al
1	0.4201	0.4324	0.1610	0.2848	0.2051	0.1296
2	0.3274	0.3119	0.1705	0.2456	0.0946	0.1035
3	0.2966	0.2197	0.1488	0.2041	0.0688	0.1123
4	0.2628	0.2226	0.1489	0.2035	0.0610	0.0961
5	0.2921	0.2771	0.2009	0.1983	0.0470	0.0723
6	0.2398	0.1775	0.1199	0.2336	0.0525	0.0602
7	0.1878	0.1412	0.1102	0.1763	0.0209	0.0660
8	0.2003	0.1499	0.1334	0.1839	0.0303	0.0776
9	0.2012	0.1195	0.1019	0.1842	0.0411	0.0681
10	0.1923	0.1405	0.1217	0.1878	0.0608	0.0982
11	0.2184	0.1550	0.0974	0.2059	0.0483	0.0872
12	0.2502	0.1723	0.1284	0.1748	0.0589	0.0537
13	0.2740	0.2189	0.1010	0.2370	0.0796	0.1009
14	0.2216	0.7808	0.8906	0.2345	0.1046	0.1116
15	0.4289	0.7394	0.3623	0.2587	0.1830	0.1157

**2.2 Distribution Law of Deposited Elements Along the Radial Direction of Catalyst**

U-shaped pattern is the major distribution form of V, Ni and S distribution along the radial direction in all of the 14 spent catalysts except a few exceptions because of

sample representativeness and analysis error. Elements distribution along the radial direction of No. 9 spent catalyst is shown in Figure 3. Elements distributions of other catalysts have a similar law.



**Figure 3**  
**Radial Distribution of Deposited Elements of No. 9 Catalyst**

The main existing forms of V in vanadium porphyrins of residue is  $(VO)^{+2}$ . V atom locates in the upward central location of a big annular plane and combined with strong polar oxygen. The strong polar oxygen can interact with catalyst surface easily, so V also has more opportunities to interact with catalyst and remove quickly. The removal rate of V is fast and Vanadium porphyrins have no chance and time to enter the interior of catalysts. Removed V inclines to deposit on the entrance of catalyst pore and shows U-shaped pattern along the radial direction. It has been confirmed and accepted by most of the researchers.

Different with the existing form of V, Ni atom locates in the center of annular plane of porphyrin. Due to the influence of polarity and steric effect, removal of Ni would take long reaction time because it is not easy to interact with catalyst. Most researchers believed that Ni inclines to deposit in catalyst interior because there is enough time to let nickel porphyrins diffuse into catalyst interior and react at the internal active site. But Al-Dalama (Al-Dalama, & Stanislus, 2006) holds that Ni is uniformly deposited in catalyst along the radial direction. Although our results are more close to the result of Al-Dalama, the Ni deposition amount is comparatively high at the entrance of catalyst pore by comprehensive analysis of Ni distributions along the radial direction of all the catalysts.

The entrance and diameter of catalyst pores are larger because there is little sediment on catalyst during the early stage of an operating cycle of commercial unit or under short-cycle operation condition in laboratory. So nickel porphyrins can diffuse into catalyst easily and be hydrotreated, which cause the high deposition amount of Ni inside the catalyst. With the increasing of operating time, the sediment on catalyst should increase, so pore diameter decrease (some pores even was blocked) and diffusion resistance increase, nickel porphyrins could not diffuse into the catalyst and hydrotreated on the outside of catalyst at the end of an operation circle. The nickel deposition of catalyst periphery was larger than that of catalyst interior on spent catalyst.

The sulfur distribution showed U-shaped pattern along the radial direction which was consistent with distribution of V and Ni. Sulfur contents changed with the changes of V and Ni contents because V and Ni were deposited on catalyst in forms of metal sulfides in residue hydrotreating.

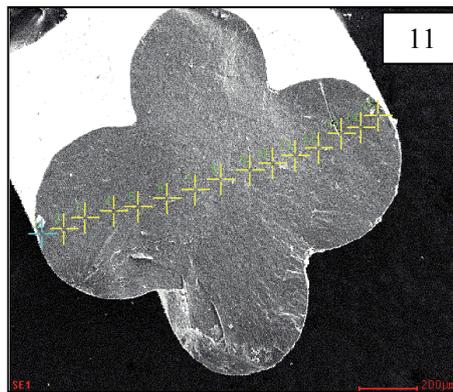
### 2.3 Relations Between Results of SEM and Element Analysis

Some connections can be found by analyze various elements contents along height of catalyst bed and the radial direction of catalyst, although element deposition amounts have not obvious change law along height of bed in commercial fixed-bed residue hydrotreating unit as a whole. The connections of SEM and element analysis are as follows:

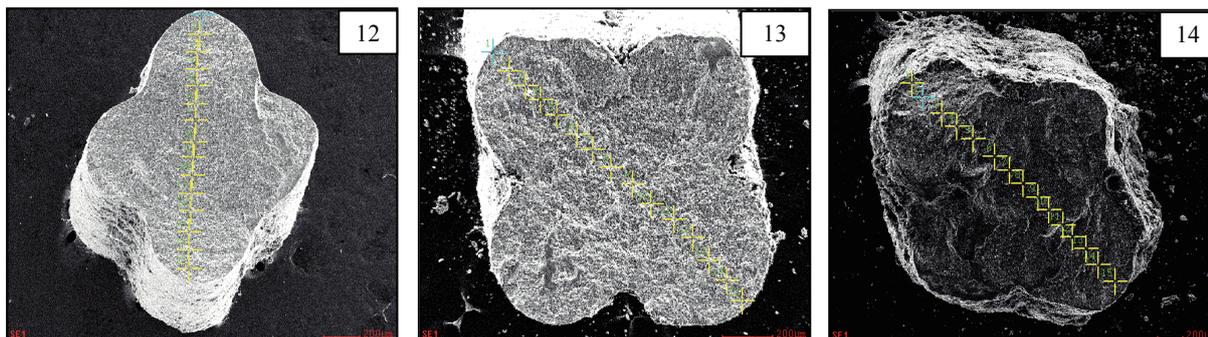
(1) Similar to results of element analysis, most of the test points with high metal content have high content of sulfur by SEM analysis. The result also further illustrates that metals deposit on residue hydrotreating catalyst in forms of metal sulfides. But there is not a fixed proportion relation between metals content and sulfur content on catalyst because different metal combined with sulfur in different states and one metal also has metal sulfides in different valence states (Toulhoat *et al.*, 1990; Grigsby *et al.*, 1997). On the other hand, besides existing in forms of metal sulfides, some organic sulfur compounds also exist in coke on catalyst. Sulfur content in coke is related to the content and existing state of sulfur in feedstocks.

(2) Similar to results of element analysis, changes of metal contents along the bed height is not obvious, although there is a decreasing tendency of metals contents. Most literatures (Sun *et al.*, 2012) believed that metals on catalyst were gradually decreased along the bed height in fixed-bed residue hydrotreating, but the change trends were not obvious according to both results of element analysis and SEM in our research. The main reason for the difference is that the research objects were small laboratory fixed-bed residue hydrotreating unit in literatures but commercial unit in our research. Different from laboratory equipment, the operating cycle of commercial units are longer, for instance, operating cycle of majority units are about one year and even up to 1.5 years. Hydrodemetalation mainly reacted at the first half part of catalyst bed because the activity of all catalyst is high in a short reaction time. Catalyst in front of the bed was gradually inactivated with the increase of reaction time, so the reaction site of hydrodemetalation shifts to rear part of the catalyst bed. The metals distribution no longer has any change law along the bed height when catalyst bed has been penetrated (and even working for a period of time after penetrated) after a period of running time.

(3) The deposited elements content on the latter catalyst even may more than that of on the former catalyst. There are two main reasons which can lead to the phenomenon. Firstly, it is related to the representativeness of catalyst samples. It is difficult to ensure that the catalyst sample can completely represent the whole situation of catalyst because only two catalyst particles of the same sample were analyzed in SEM analysis. The result further explains that the property changes of catalyst were uncertain in residue hydrotreating reactor. Secondly, it was found that the external structure of high metal deposition catalyst have all changed obviously (the internal structure can not observe clearly) according to observe and analyze SEM image. Comparing with other catalysts, the structure of high metal deposition catalyst was destroyed obviously or massive irregular material have deposited on the external surface of high metal deposition catalyst (see Figure 4 and Figure 5). There is significant difference between the two kinds of catalyst.



**Figure 4**  
**SEM Image of Normal Catalyst**



**Figure 5**  
**SEM Images of High Deposition Catalysts**

## CONCLUSIONS

(1) Different from laboratory equipment, V, Ni and S showed U-shaped pattern along the radial direction of spent catalysts of commercial residue hydrotreating unit.

(2) The catalyst bed has been penetrated by deposited metals and deposited massive metals on catalyst at the end of an operation cycle. The reactants entered inside of catalysts more difficultly (even impossible) because the pore had been blocked by sediments to let diffusion resistance increased. Most of the organometallic compounds hydrotreated and deposited on outside of catalyst particles at the end of operation cycle.

(3) Metals deposit on residue hydrotreating catalyst in forms of metal sulfides. But there is not a fixed proportion relation between metals content and sulfur content on catalyst.

(4) The structure of high metal deposition catalyst was destroyed obviously or massive irregular material have deposited on the external surface of high metal deposition catalyst.

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