



## Demetallization by MCM-48 from Asphalten of Vacuum Residual Oils: Analysis by UV-Visible Spectrophotometer†

HEON CHANG KIM, WON JAE JEONG, WHO CHUL LEE and SEUNG KYU PARK\*

Department of Chemical Engineering, Hoseo University, Asan 336-795, Republic of Korea

\*Corresponding author: Fax: +82 41 5405758; Tel: +82 41 5409686; E-mail: [skpark@hoseo.edu](mailto:skpark@hoseo.edu)

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In this study, MCM-48 shows the effective elimination of Ni(II) among several adsorbents from asphalten of vacuum residual oils. The elimination can be monitored by the absorption of UV-visible spectrophotometer and time-of-flight secondary ion mass spectrometry (SIMS-TOF). The combination of the analysis of UV-visible spectroscopy and SIMS-TOF analysis provide the concrete evidence for the elimination of vanadium and sulfur from the asphalten part of heavy residual oil through the adsorption process onto MCM-48 adsorbent.

**Keywords:** Ni, MCM-48, Heavy vacuum residual oil, UV-visible spectroscopy, SIMS-TOF.

### INTRODUCTION

Some transition metals such as Ni(II) and V(II) materials in the heavy vacuum residual oil fractions are difficult to be eliminated since they exist as metal-porphyrin complex<sup>1</sup>. Crude oil is composed of hydrocarbons, however also containing sulfur, nitrogen and transition metals<sup>2</sup>. After the fractional distillation of crude oil, most of the transition metals remain to the heavy vacuum residual oil<sup>3,4</sup>. The heavy vacuum residual oil have been recognized as low grade oil and consumed as fuel of industrial boiler, in part. The amount of metals in crude oil usually varies from a few parts per million to more than 1000 ppm<sup>5,6</sup>. Usually they are in an oil-soluble form and become concentrated in the heavy vacuum residual oil fractions in conventional refining processes. Among these metals the most abundant and undesirable are nickel and vanadium. The Ni and V in the heavy residue cause corrosion problems by formation of metal oxide in the combustion chamber. When the mixture of the heavy residual oil and bunker C oil is applied to fuel, the metals in the mixed oil could increase of gas and coke formation and decrease the yields of gasoline. These metals in the heavy residue cannot be eliminated by simple chelation process since they are known to be existed as very stable structure such as metal-porphyrins<sup>1,6</sup>.

A number of authors have attempted to quantify metalloporphyrins in crude oil by using the extinction coefficients of isolated V(II) compounds or model compounds. Freeman and

O'Haver applied derivative UV/visible spectroscopy to quantify the concentration of metalloporphyrins in de-asphalted bitumen samples<sup>7</sup>. They found significant absorbance by non-porphyrinic compounds in the region of the solet band at around 400 nm and therefore had to resort to using the  $\alpha$  band. In order to counteract the reduced sensitivity of this peak, data smoothing and second derivative algorithms were applied to the spectrum. These data analysis algorithms serve to improve the signal-to-noise ratio, which is a major difficulty when dealing with complex mixtures where significant background absorbance is present. In the end, they concluded that the optimal algorithm was a second derivative, 3 point sliding average algorithm. Ferrer and Baran<sup>8</sup> extended this analysis further by applying third derivative UV/visible spectroscopy for the qualitative identification of metalloporphyrins. The use of the third derivative of the absorbance allows for a much more precise identification of the exact wavelength (to within  $\pm 0.1$  nm) of an absorbance maximum since the third derivative is characterized by a steep zero crossing at an absorbance peak. This method allowed the investigators to differentiate a number of different metalloporphyrins on the basis of the UV/visible spectra alone. This method requires that the petroporphyrins be separated and/or purified prior to analysis. In this research, the nickel and vanadium metals in the vacuum residue have been eliminated by the combination of solvent separation process and chelating process<sup>6,8</sup>. The solvent separation process is capable of removing all or a substantial amount of metals

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from the vacuum residues that are destined for further processing such as in the middle of refining step.

In this study, UV-visible spectrophotometric analysis is applied for the determination of Ni and V contents in the heavy vacuum residual oil. They are extracted into a solid sorbent matrix such as MCM-48 at asphalted phase in the heavy vacuum residual oil with a colorimetric reagent and then quantified directly using by diffuse reflectance UV-visible spectrophotometer. The analysis of surface composition of the transition metal trapped MCM-48 by SIMS-TOF provides the direct evidence for the elimination of Ni and V in the asphalted phase of the heavy vacuum residual oil<sup>9,10</sup>.

## EXPERIMENTAL

The composition of vacuum residual oil provided by SK Energy in Korea was revealed to be saturates (5 %), aromatics (65.8 %), resins (15.4 %) and asphaltting (13.8 %) by SARA analysis. MCM-48 was synthesized using a sodium silicate solution as the silica source, hexadecyltrimethylammonium bromide (HTABr) as the templating agent and as an additive for the mesophase control<sup>11,12</sup>.

**Analysis of transition metals:** The elimination of transition metals such as Ni(II) and V(II) has been tested by adsorption onto several adsorbents including MCM-48. The 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (Br-PADAP) solution (0.025 %) was prepared by dissolving 0.063 g (Aldrich) in 10 mL of ethanol and 100 mL of Triton X-100 solution (8 %) and dissolution up to 250 mL with deionized water. The Br-PADAP reacts with nickel(II) in the presence of Triton X-100 to form a complex with absorption maxima at 530 and 562 nm. In the pH range 5-6, nickel reacts with 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol to form a red-violet complex which has two absorption maxima, at 520 and 560 nm. The concentration of Ni can be monitored by the absorbance at 546 nm of UV-visible spectrophotometer in this work. The standard calibration result demonstrated that using the derivative technique, Br-PADAP can be used for nickel determination with selectivity higher than that of ordinary spectrophotometry. The buffer solution was prepared by adding of 103.3 g of sodium acetate trihydrate and 14.1 mL of acetic acid and dissociation up to 1 L with deionized water.

Time-of-flight secondary ion mass spectrometry (SIMS-TOF) is a surface-sensitive analytical method that uses a pulsed ion beam (Cs or microfocused Ga) to desorb and ionize molecules from the surface of the sample. The particles are removed from atomic monolayer on the surface and then accelerated into a flight tube. Their mass depending on the weight is determined by measuring the exact flight time.

## RESULTS AND DISCUSSION

Buffered solutions with nickel(II) concentrations between 40 and 160 ppm were passed through the cartridge/holder unit. The obtained absorbance (A.U) responses at 540 nm are plotted against sample concentration in Fig. 1. The wavelength of detection is the maximum of the Kubelka-Munk function for the precipitate. Initial experiments that utilized the reagent chad as a means of introducing dimethyl glyoxime to the sample were conducted with 3 mL buffered nickel(II) solutions and

demonstrated a clear trend between the absorbance (A.U) value at 540 nm and nickel(II) concentration as shown in the calibration curve in Fig. 1.

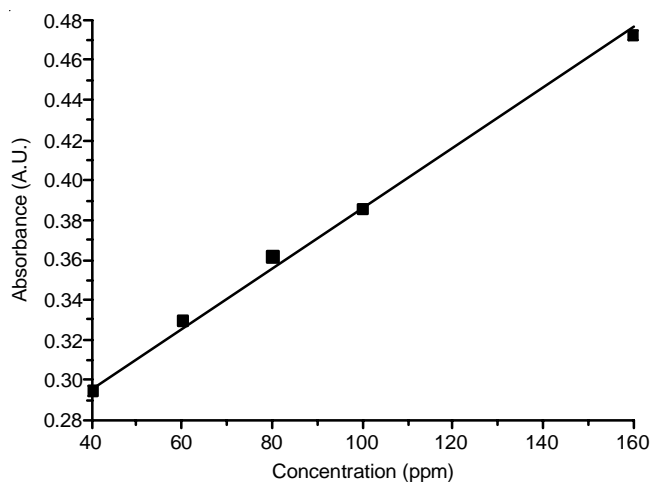


Fig. 1. Calibration curve for nickel(II) in buffered sample solution obtained by UV-visible photometer

Buffered solutions with nickel(II) concentrations between 40 and 160 ppm were passed through the cartridge/holder unit. The obtained absorbance (A.U.) responses at 540 nm are plotted.

Fig. 2 shows the elimination of Ni(II) from the solution after the application onto MCM-48. The absorbance of the complex reaches a stable region after 10 min adsorption onto MCM-48. The nickel concentration adsorbed onto MCM-48 increases as the MCM-48 concentration increases. Ni elimination from the reagent is maximized (> 95 %) after 30 min of mixing the reagents and is stable for at least 24 h.

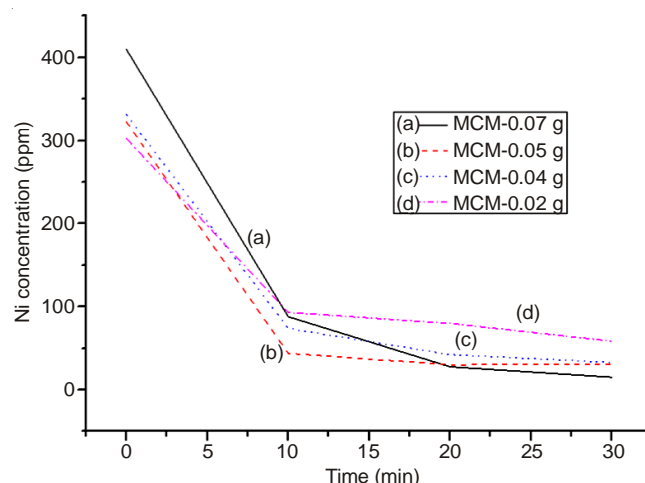


Fig. 2. Elimination of Ni(II) from the asphalten solution after the application onto MCM48

Fig. 3 shows the morphology and composition of the surface after adsorption of Ni(II) onto MCM-48 from the solution by SIMS-TOF analysis method. After the adsorption reaction of asphalten-toluene solution and MAM-48 (0.07 g) for 0.5 h at room temperature, the surface of MCM-48 was analyzed by SIMS-TOF. The transition metals were gradually adsorbed onto the surface of MCM-48. Nickel and sulfur

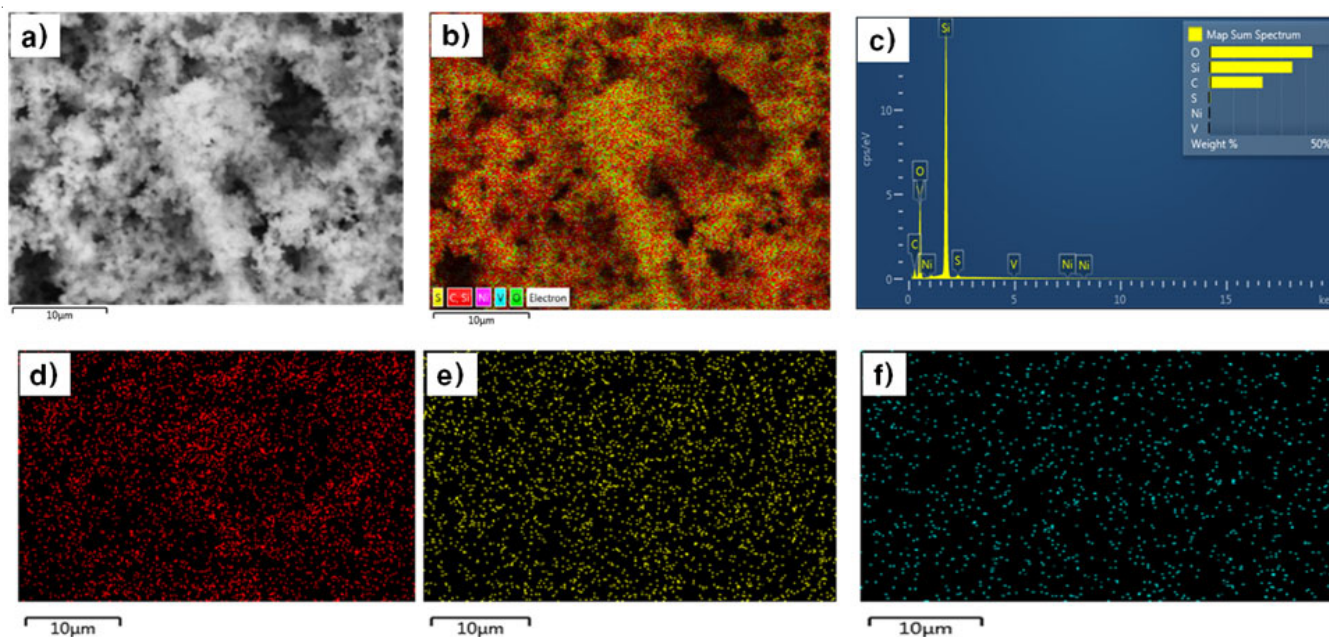


Fig. 3. Surface analysis by SIMS-TOF (a) MCM-48 surface electron image of MCM-48, (b) Surface EDS image of MCM-48, (c) Element analysis results, (d) Carbon element on the MCM-48, (e) S element on the MCM-48 and (f) Ni on the MCM-48 after the adsorption reaction of asphalten with MCM-48 (0.07g) for 0.5 h

concentration were increased as the adsorption onto the sorbents proceeded. For the adsorption of Ni(II) onto MCM-48, the Ni(II) adsorption onto MCM-48 obtained by UV-visible spectrophotometer shows statistically same results analyzed by ICP method or SIMS-TOF analysis method.

On the basis of SIMS-TOF analysis, the surface composition of MCM-48 was Si (34.5 %): O (42.8 %): C (22.2 %): S (0.44 %): Ni (0.02 %). Since carbon, sulfur and nickel are observed on the surface of MCM-48, we suggest that Ni-porphyrin is adsorbed on MCM-48. Furthermore, the combination of the analysis of UV-visible spectroscopy and SIMS-TOF analysis provide the concrete evidence for the elimination of vanadium and sulfur from the asphalten part of heavy residual oil through the adsorption process onto MCM-48 adsorbent.

### Conclusions

A new strategic analysis of transition metal sequestering to sorbents by UV-visible spectrophotometer and SIMS-TOF analysis method is developed. In this research, the elimination of nickel and sulfur has been studied by solvent distillation and MCM-48 sequestering process. The solvent separation process is capable of removing all or a substantial amount of metals from the vacuum residues that are destined for further processing such as in the middle of refining step. About 95 % of Ni in the insoluble portion of asphalten can be eliminated by treatment of MCM-48. Furthermore, the combination of the analysis of UV-visible spectroscopy and SIMS-TOF

analysis provide the concrete evidence for the elimination of vanadium and sulfur from the asphalten part of heavy residual oil through the adsorption process onto MCM-48 adsorbent.

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