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Research Article

Application of a New Method in Identifying the Sludge Deposits from Refineries and Gas Plants: A Case of Laboratory-Based Study

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This article reports the application of a new method in identifying the accumulated sludge deposits (e.g., oily sludge, water sludge, and filter sludge). The method is an excellent approach for identifying the inorganic materials found in sludge deposits generated in refineries and gas plants. The phase identification and quantification on inorganic material in the form of corrosion products are important to facilitate chemical cleaning and prevent the reoccurrence to stop the generation of sludges. Therefore, the authors developed a new method to separate the inorganic materials from the hydrocarbon of the as-received sludge samples from the fields. When the sample preparation was taken with great care, the results revealed that this method is fast and can accurately identify very small quantities (>0.5 wt%) of sludge deposits present in the sample. Additionally, if the color of the dichloromethane soluble part collected is changed, it indicates the presence of hydrocarbon in the sludge. Thermal gravimetric analysis results revealed that the sludge contained approximately 3 wt% of inorganic compound, 25 wt% of water, and 72 wt% of hydrocarbon. Subsequently, gas chromatography mass spectrometry analysis results revealed that the type of hydrocarbon was diesel with the C10–C27.

1. Introduction

Sludge deposits are the semisolid mixture and formed by the combination of liquid (e.g., oil and water), hydrocarbon (e.g., grease and lubricant), and nonhydrocarbon or inorganic compounds of solids [1, 2] in the forms of scale deposits and corrosion products. The sludge deposits, which are mixture of solid and viscous material, are formed at the different parts of equipment in refineries and gas plants. For example, Figure 1 shows the sludge deposits that are formed by the combination of inorganic compounds in the forms of corrosion products, scale, and chemicals with hydrocarbons, such as oil, lubricant, grease, and water or all. These sludge deposits are either generated in the particular equipment or carried over from another source.

In this paper, a new method was developed in separating the nonhydrocarbon or inorganic materials from the hydrocarbon parts of the accumulated sludge deposits (e.g., oily sludge, water sludge, and filter sludge) in refineries and gas plants. For example, a known quantity of sludge deposits was taken in a beaker and dried in a fume hood for 2 to 3 days for water-based sludge. Figure 2(a) shows the oil-based sludge that was treated with dichloromethane and then filtered in the filtration assembly. Additionally, Figure 2(b) depicts the insoluble part for inorganic materials that was measured by X-ray diffractometer and analyzed by the High Score Plus software to determine the phase identification of the X-ray powder diffraction (XRD) data of the crystalline materials at the treated sludge samples. The new method is an excellent approach for identifying the inorganic materials found in sludge deposits generated in refineries and gas plants.

XRD peaks are produced by constructive interference of a monochromatic beam of X-rays scattered at specific angles from each set of lattice planes in a sample [3]. The peak intensities are determined by the distribution of atoms within the lattice. Consequently, the XRD pattern is the fingerprint of periodic atomic arrangements in a given material. Additionally, the XRD differentiates between different forms

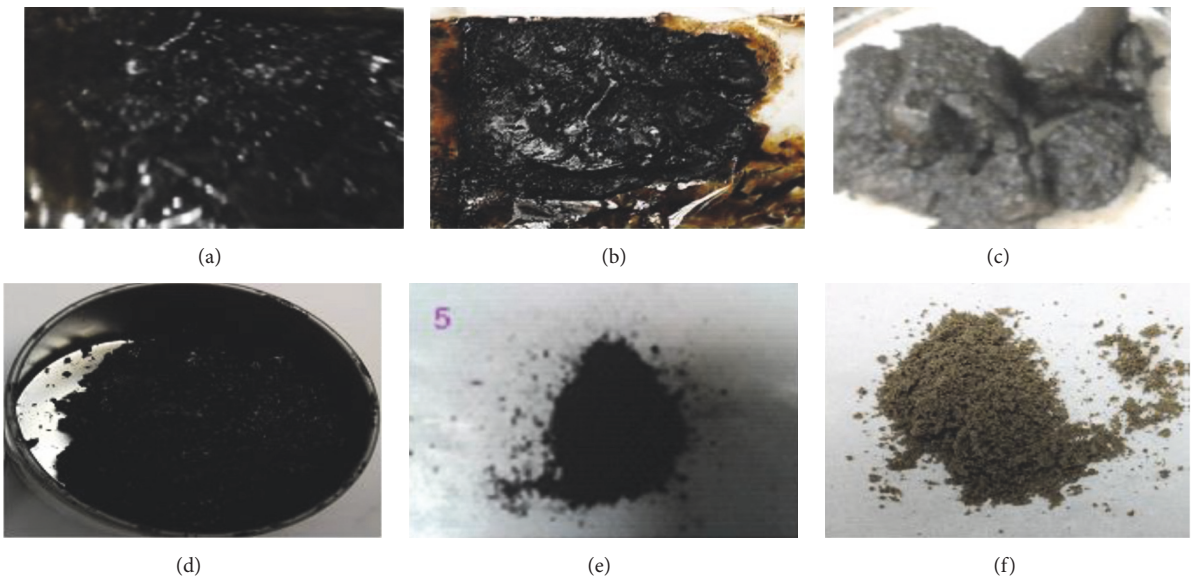


Figure 1: The schematic diagrams of the sludge samples used in this study are (a) oily sludge, (b) soft sludge, (c) water sludge, (d) dry oily sludge, (e) filter sludge, and (f) dry soft sludge.

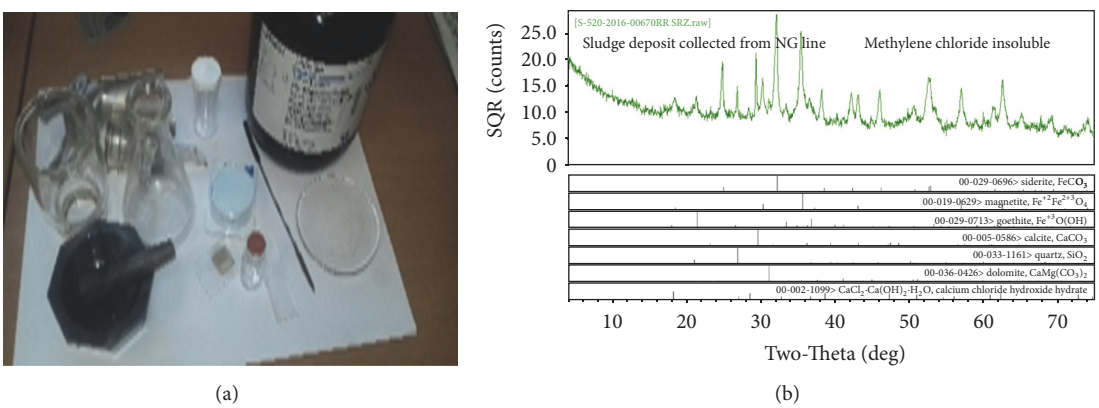


Figure 2: (a) The schematics of dichloromethane, filtration assembly, mortar pestle, filter paper, beaker, spatula, and container. (b) Phase identification results of sludge deposit collected from the NG line, where the methylene chloride was insoluble.

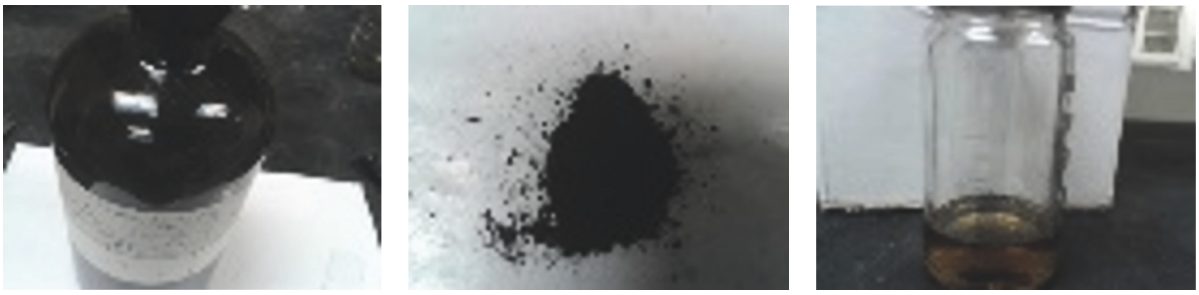
of phases and/or crystal structure with the same chemical formulae [3–6]. Therefore, it is an excellent method for identifying the inorganic materials found in sludge deposits generated in refineries and gas plants [7]. If the sample preparation is taken with great care, XRD provides accurate information on phase identification [8], Figure 2(b).

When all the phases are identified accurately, the Rietveld method [9–11] can be used to perform the crystal structures [12], crystallographic preferred orientations [13], and quantitative phase analysis [14–17] of XRD data of crystalline materials. Additionally, the other structural parameters, such as average grain size, crystallinity, strain, and crystal defects can also be determined if they are required. Rietveld analysis adjusts the refinable parameters until the best fit of the entire calculated pattern to the entire measured XRD pattern is achieved. Moreover, the Rietveld analysis does not require measurement of calibration data, nor the use of an internal standard. Consequently, it requires the crystallographic information file (e.g., crystal structures) for each of the identified phases before conducting the refinements.

The main objective of this laboratory-based study was to develop a method that can identify precisely the sludge deposits that align with the need of XRD applications in refinery and gas plants. When the sample preparation was taken with great care, this new method is fast and accurate to identify more than 40 samples from the refineries and gas plants, which are very small quantities (>0.5 wt%) of corrosion products, scale deposits, inorganic additives, and so forth, in sludge deposits.

2. Experimental Methods

To fulfill the above objectives, in the present study, the authors developed the new method and assessed it experimentally



(a) (b) (c)

Figure 3: The schematic of the unknown black sludge deposit that was found in the diesel oil tank in a refinery: (a) the as-received sample, (b) dichloromethane insoluble, and (c) dichloromethane soluble.

on the various sludge samples, Figure 1. These samples were collected from many different locations in refineries and gas plants.

2.1. A New Method Developed in Sample Preparation Procedures. Listed here are the new methods in sample preparation to identify the accumulated sludge deposits from refineries and gas plants and assessed it for each of the as-received sludge samples:

(1) For the water-based sludge, a known quantity of sludge was taken in a beaker and dried in a fume hood for 2 to 3 days.

(2) For sulfur analysis, it is a must to analyze samples without any pretreatment.

(3) For oil-based sludge, it was treated with dichloromethane and then filtered in the filtration assembly, Figure 2(a). If hydrocarbon is present in the sludge, the color of the dichloromethane soluble part collected is changed.

(i) The dichloromethane insoluble part (i.e., inorganic materials or nonhydrocarbon) was analyzed by XRD for inorganics, Figure 2(b).

(ii) The dichloromethane soluble part (i.e., hydrocarbon) was analyzed by gas chromatography mass spectrometry, Figure 5.

2.2. XRD Data Measurements, Phase Identification, and Quantification. The treated samples previously described in the sample preparation procedures were manually ground by an agate mortar and a pestle for several minutes to achieve a fine particle size [12], Figure 2(a). Then, the fine powders were mounted into the sample holders by front pressing. Furthermore, high-resolution XRD data of the samples were measured using the Rigaku ULTIMA-IV XRD with a copper X-ray tube from 4° to 75° 2θ Bragg-angles with a step size of 0.04° and counting time of 1° per minute.

In this article, the authors used the software package PANalytical High Score Plus (X'Pert High Score Plus Version 2.2c PANalytical Inc.), combined with the ICDD of the PDF-4+ database of the standard reference materials to determine the phase identification of the XRD data of the crystalline materials at the treated sludge samples. Subsequently, the Rietveld method was used to refine whole XRD patterns for the phase composition analysis [14–17] (i.e., wt% for each of the identified phases). The parameters refined for the random orientation of crystallites were the same as those described by Sitepu et al. [12].

3. Results and Discussions

3.1. The Application of the New Method in Identifying the Sludges Deposit That Was Found in the Diesel Oil Tank in a Refinery: A Case of Laboratory-Based Study. To assess further the new method, the authors particularly investigated the unknown black sludge deposit that was found in the diesel oil tank in a refinery, a case study. Figure 3 shows the schematics of the unknown black sludge deposit, which was found in the diesel oil tank in a refinery. The sludge composition obtained from this new method was sought to determine their nature and source to stop its reoccurrence.

Figure 4 shows XRD patterns of the as-received black sludge deposits that were found in the diesel oil tank in a refinery and sludge sample after removing the hydrocarbon. It can be seen from Figure 4(a) that the measured XRD pattern of the as-received sample is mainly mixed between the amorphous with the small addition of crystalline materials. Subsequently, after removing the hydrocarbon, XRD pattern of the inorganic materials shows that the sample is the crystalline materials with a reasonable peak and background ratio for phase identification purposes, Figure 4(b). When the XRD data of the inorganic materials were identified by the High Score Plus software, the results revealed that the inorganic materials consist of iron oxide in the form of goethite [FeO(OH)], magnetite [Fe_3O_4], and lepidocrocite [FeO(OH)], iron sulfide in the form of pyrite [FeS_2] and pyrrhotite [$Fe_{1-x}S$], and quartz [SiO_2]. Subsequently, when the XRD data of the identified phases were refined using the Rietveld method, the results revealed that the inorganic materials consist of 82 wt% of iron oxide in the form of 56 wt% goethite [FeO(OH)], 15 wt% of magnetite [Fe_3O_4], and 11 wt% of lepidocrocite [FeO(OH)]; 16 wt% of iron sulfide in the form of 15 wt% of pyrite [FeS_2] and 1 wt% of pyrrhotite [$Fe_{1-x}S$]; and 2 wt% of quartz [SiO_2].

The hydrocarbon appeared in the sludge deposits because the color of the dichloromethane soluble part collected was

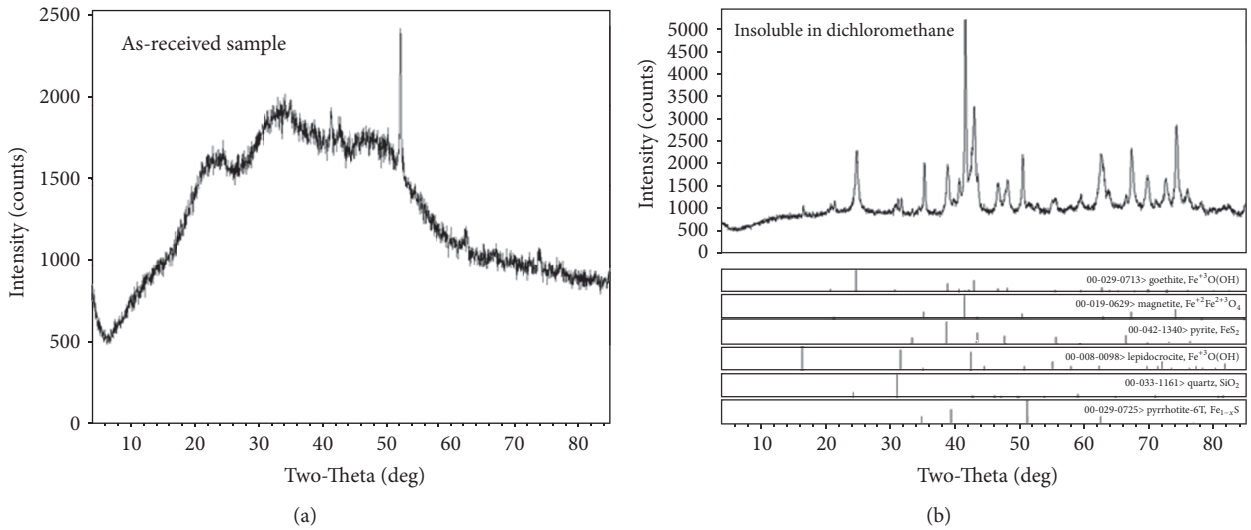


Figure 4: XRD data of the sludge sample: (a) as-received (i.e., mix between the amorphous with the small addition of crystalline materials) and (b) after removing the hydrocarbon (i.e., inorganic materials).

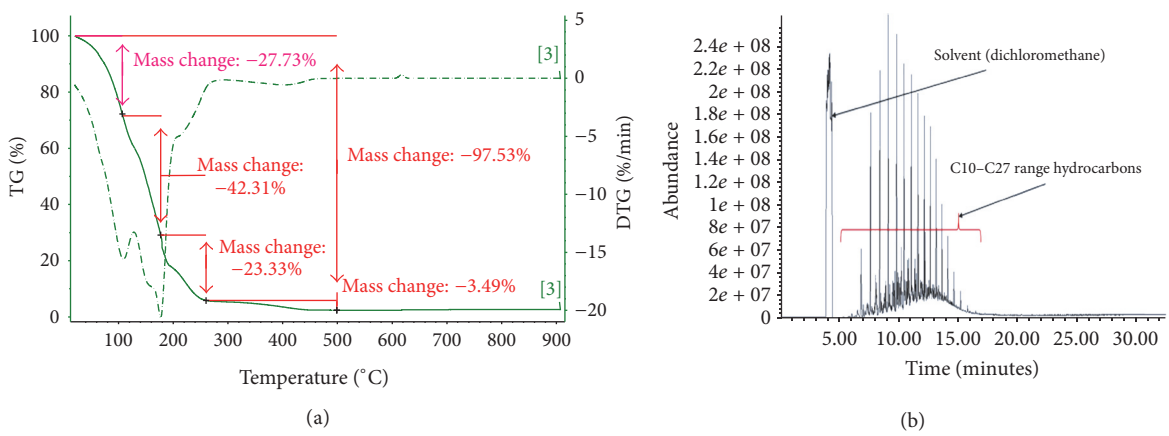


Figure 5: (a) The thermal gravimetric analysis and (b) gas chromatography mass spectrometry results.

changed. Therefore, the wt% of hydrocarbon and water and the type of hydrocarbons were determined by thermal gravimetric analysis and gas chromatography mass spectrometry, respectively. Figures 5(a) and 5(b) show the thermal gravimetric analysis and gas chromatography mass spectrometry of the sample, respectively. When the thermal gravimetric was used to analyze the sample, the results revealed approximately 3 wt% of inorganic compound, 25 wt% of water, and 72 wt% of hydrocarbon content, Figure 5(a). Subsequently, when gas chromatography mass spectrometry was used to analyze the sample, the results revealed that the hydrocarbon type was diesel with the C10–C27, Figure 5(b).

The application of the new method has been extended to identify 40 sludge samples. Table 1 and Figures 6, 7, 8 and 9 show the phase identification results obtained from High Score Plus of the XRD data of the sludge deposits, which are either generated in the particular equipment in refineries and gas plants or carried over from another source.

It can be seen from Figure 6(a) that the XRD pattern of the as-received scale sample from the crude oil booster pump are mixed between the amorphous and crystalline materials. Additionally, the background is high, and therefore, the peak to background ratio is low. Figure 6(b) depicts the XRD pattern of the same sample after removing the hydrocarbon. It is interesting to note that here the amount of the inorganic material was relatively small. It can be seen clearly from Figure 6(b) that the sample has crystalline materials with a very high peak to background ratio, which means that the High Score Plus software has provided an accurate phase identification of this reasonable XRD data. All phases were identified in this sample; they are halite [NaCl], thermonatrite [$Na_2(CO_3)H_2O$], and natrite [$Na_2(CO_3)$]. Therefore, it indicates that if the sample preparation of the sludge sample was taken with great care, for example, follow the five steps of the previously mentioned sample preparation procedures, XRD provides high precision results of phase identification. The findings show that the new method accurately identified

Table 1: Summary of sludge chemical compounds obtained from High Score Plus.

The identified compounds	Nature
Barite-$BaSO_4$	Drilling mud
Quartz-SiO_2 Albite-$NaAlSi_3O_8$ Microcline-$KAlSi_3O_8$ Cristobalite-SiO_2	Formation material, normally found in the sandstone or sand
Illite-$K_{0.5}(AlFeMg)_3(SiAl)_4O_{10}(OH)_2$	Clay minerals normally found with sandstone
Magnetite-Fe_3O_4 Lepidocrocite-FeOOH Goethite-FeOOH Akaganeite-FeOOH	Corrosion product: at high temperature magnetite corrosion products it will coat the iron/steel to prevent oxygen to reach underlying metal. Mostly, at low temperature lepidocrocite formed and with time it transformed into most stable goethite. Akaganeite formed in marine environments
Basanite-$CaSO_4{\cdot}2H_2O$ Anhydrite-$CaSO_4$ Gypsum-$CaSO_4{\cdot}2H_2O$	Sulfate scale
Ettringite-$Ca_6Al_2(SO_4)_3(OH)_{12}$	Cementing material
Aluminum Oxide-Al_2O_3	Normally from catalyst
Gregite-Fe_3S_4 Pyrite-FeS_2 Marcasite-FeS_2 Mackinawite-$FeS_{0.9}$ Pyrrhotite-Fe_7S_8	Corrosion products: pyrophoric iron sulfide (pyrrhotite-FeS) results from the corrosive action of sulfur or sulfur compounds (H_2S) on the iron (steel) and moisture
Sulfur-S	
Sodium Iron Oxide-$NaFeO_2$	
Calcite-$CaCO_3$ Aragonite-$CaCO_3$ Siderite-$FeCO_3$	Carbonate scale
Iron Chloride-$FeCl_3$ Iron Chloride Hydrate-$FeCl_2$-$4H_2O$	Chloride corrosion products

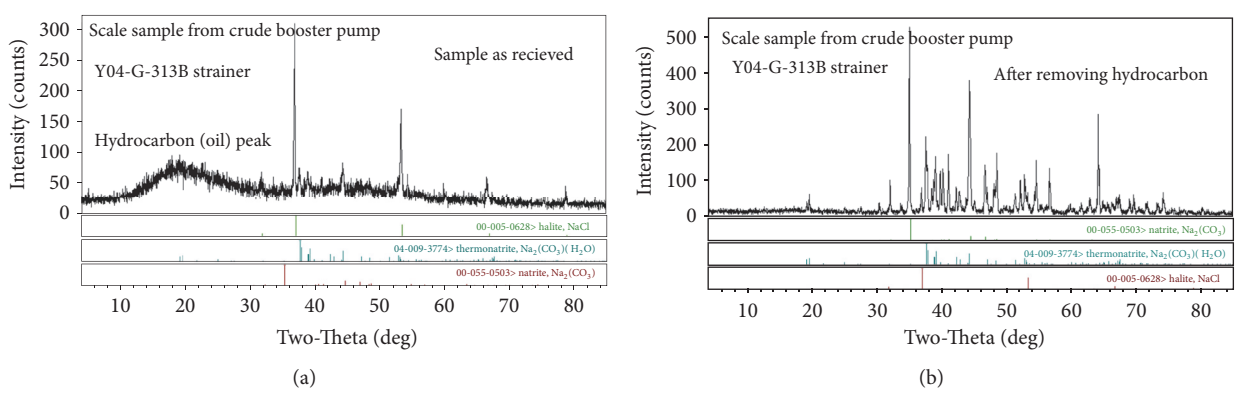
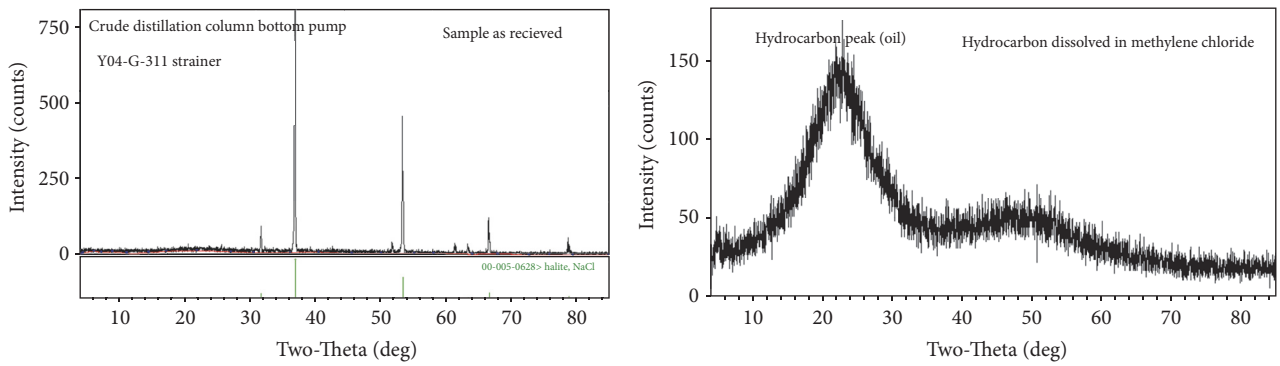


Figure 6: Phase identification results of the scale sample from crude booster pump: (a) the as-received and (b) after removing hydrocarbon along with the standard reference minerals for halite (NaCl), thermonatrite ($Na_2(CO_3)H_2O$), and natrite ($Na_2(CO_3)$).

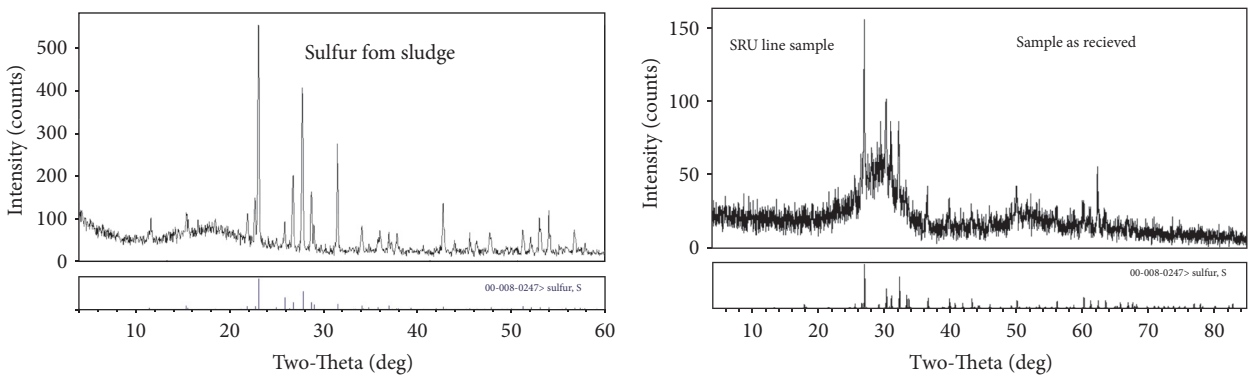
very small quantities (>0.5 wt%) of scale deposits present in the samples, Figures 7(a), 8(a), and 9(b). On the other hand, Figures 7(b), 8(b), and 9(a) show the XRD patterns of the as-received sludge deposits before treating, which mainly consists of amorphous materials, indicating that they are hydrocarbon compounds.

Figure 2(b) shows the phase identification of the XRD data of sludge deposit collected from the NG line, which shows the methylene chloride as being insoluble. There are seven phases detected, siderite [$FeCO_3$], magnetite [Fe_3O_4], goethite [FeO(OH)], calcite [$CaCO_3$], quartz [SiO_2], dolomite [$CaMg(CO_3)_2$], and calcium chloride hydroxide hydrate [$CaCl_2{\cdot}Ca(OH)_2{\cdot}H_2O$]. It can be seen from Figure 4 that the new sample preparation method developed in this study provides good XRD data of the small amount of the inorganic material. Therefore, the sample preparation of the sludge deposit has to be taken with great care to obtain a good XRD pattern and the High Score Plus software will



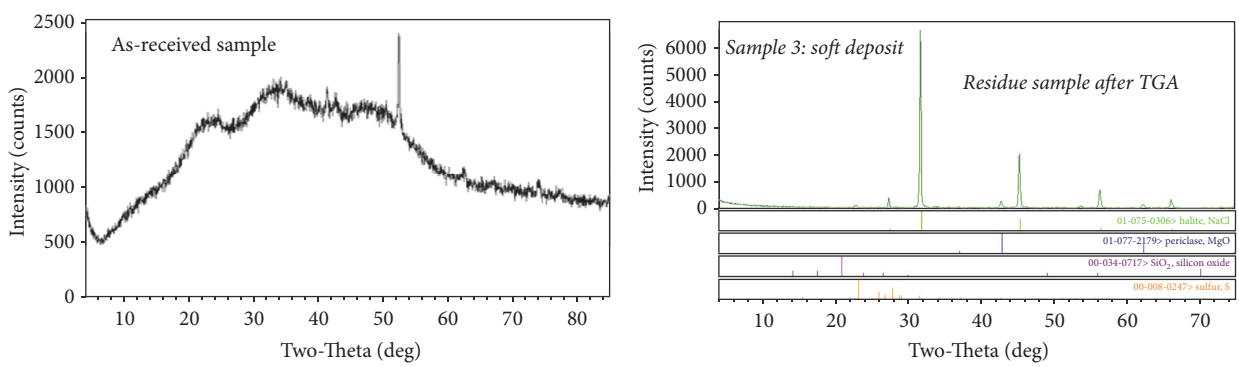
(a) Crude distillation column bottom pump (b) The hydrocarbon materials

Figure 7: XRD phase identification results along with the standard reference mineral. (a) The as-received, crude distillation column bottom pump consists of halite [NaCl]; (b) the sludge, which shows the hydrocarbon peak. Here hydrocarbon is dissolved in methylene chloride.



(a) (b)

Figure 8: XRD phase identification results along with the standard reference minerals of the sulfur from the (a) sludge and (b) recovery unit line.



(a) (b)

Figure 9: XRD phase identification results along with the standard reference mineral. (a) The sulfur recovery unit 1 and (b) the residue soft deposit sample after thermal gravimetric analysis along with the identified phases, halite [NaCl], periclase [MgO], silicon oxide [SiO_2], and sulfur.

provide high precision results of the phase identification. The findings show the new method accurately identified very small quantities (>0.5 wt%) of sludge deposits present in the sample. Additionally, the findings help the field engineers to facilitate efficient cleaning of the equipment and prevent their reoccurrence to avoid plant slowdown that resulted in loss of production.

4. Conclusions

Based on the findings from this new sample preparation method, the following conclusions can be drawn:

(1) The new method is an excellent technique for identifying the inorganic materials found in sludge deposits generated in refineries and gas plants.

(2) When the sample preparation was taken with great care in the present study, this method is fast and can accurately identify very small quantities (>0.5 wt%) of corrosion/scale deposits, inorganic additives, chemicals, catalysts, formation materials, clay minerals, and drilling muds present in the sample.

(3) If hydrocarbon appeared in the sludge deposits, the color of the dichloromethane soluble part collected was changed.

(4) Thermal gravimetric analysis results revealed that the sludge contained approximately 3 wt% of inorganic compound, 25 wt% of water, and 72 wt% of hydrocarbon.

(5) Gas chromatography mass spectrometry analysis results revealed that the type of hydrocarbon was diesel with the C10–C27.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

Acknowledgments

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