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# THE CHARACTERIZATION OF CRYSTALLINE DEPOSITS FROM THE FIELD BY QUANTITATIVE RIETVELD PHASE ANALYSIS

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## *ABSTRACT*

*In this paper, the authors report quantitative Rietveld phase analysis or weight percentage (wt%) for each of the identified crystalline phases of deposits from the field. The objectives of the study were to quickly, precisely and accurately identify the phases appear at the very tiny amount of the crystalline deposits that were build up in the specifics affected systems. Subsequently, when all of the phases were identified (finger prints or qualitative analysis), quantitative Rietveld phase analysis was used to determine of weight percentage for each of the identified phases. The results revealed that iron oxide corrosion products mainly present at the affected equipment in a refinery, which suggests that at low temperature the mostly formed and with time lepidocrocite iron oxide corrosion products transformed into most stable goethite phase, which is the other types of iron oxide corrosion products with a different crystal structure. Subsequently, iron sulfate corrosion products mainly appeared at the tiny crystalline deposits part collected from sulfur recovery unit. The findings help the field engineers and scientists in taking the right procedures on how to prevent the accumulated deposits at particular affected equipment.*

***KEYWORDS:*** *Quantitative Rietveld phase analysis, crystalline deposits, XRD*

## INTRODUCTION

The frequently scale and corrosion sludge deposits build up in the specifics affected system scan cause failures the equipment[1,2,3]. Sitepu and Zaidi (2017)[3] successfully separated the crystalline materials (non-hydrocarbon part) from the non-crystalline materials (or amorphous – hydrocarbon part) of the sludge deposits collected from the particular failure equipment at refinery and gas plants; and quickly and accurately calculated the weight percentage for each of the identified phases by Rietveld method. The research findings help the engineers and scientists at the field[1–3] to

- Determine the source and nature of the deposits;
- Facilitate chemical cleaning[1] if requires; and
- Avoid these accumulated deposits inside the particular failure equipment.

To achieve the accuracy and reproducibility of the results for quantitative phase analysis by Rietveld method, the authors extend the research conducted by Sitepu et al. (2005 & 2015) and Sitepu (2019). Noted, that, reference intensity ratio only relies on the strongest single peak, whereas the Rietveld method uses whole pattern fitting. Additionally, Rietveld analysis adjusts the refinable parameters until the best fit of the whole calculated pattern to the entire measured X-ray powder diffraction (XRD) pattern is achieved and converged (Sitepu et al., 2005; Sitepu, 2009). Quantitative phase

analysis by Rietveld method[10–13] determine the weight percentage ($W_p$), for each of the identified phases from whole powder XRD data of crystalline deposits ($p$) according to the following equation:

$$W_p = s_p(ZMV)_p / \sum_{i=1}^{n} s_i(ZMV)_i$$

where, $Z$ is the number of formula units per unit cell, $M$ is the mass of the formula unit, and $V$ is the unit-cell volume (in Å$^3$). In crystal structure, texture and phase composition determination, there are at least five advantages of the Rietveld method[13] compare to the reference intensity ratio method. They are:

- $Z$, $M$, and $V$ values, which are the calibration constants, are calculated from whole-powder diffraction pattern rather than by laborious experimentation,
- Irrespective of overlap, whole XRD intensities are explicitly included in the Rietveld refinement,
- The background of the data is accurately and precisely defined,
- The whole XRD intensities can be corrected due to the effects of crystallographic preferred orientation[5], which can cause serious systematic errors in quantitative phase analysis and crystal structure refinement, and determined, and
- Both the atomic positions including cell-parameters, and pseudo-Voight peak-profile parameters are refined as part of the same structural, texture and phase composition determination by Rietveld analysis.

The objective of this paper was to assess and extend the new method developed by Sitepu et al. (2005) and Sitepu and Zaidi (2017)[3] to quickly, precisely and accurately determine the quantitative Rietveld phase analysis of the very tiny crystalline deposits collected from the particular failure equipment. The findings can help the engineers and scientists at the field to overcome the reoccurrence of the sludge deposits at the specific affected equipment.

## EXPERIMENTAL PROCEDURE

In the present study – the sample preparation method developed by Sitepu and Zaidi (2017)[3] has been extended to (i) separate the crystalline materials from the non-crystalline or amorphous (hydrocarbon part) of the sludge deposits collected from different failure equipment in sulfur recovery unit, and (ii) characterize the very small quantities of the crystalline inorganic part present in the deposits.

In this paper, the authors described two cases of laboratory-based studies. They are the quantitative Rietveld phase analysis of the whole pattern of the very tiny crystalline deposits part present at sludge deposits that were collected from a refinery and the process equipment. The findings help the field engineers and scientists to stop the reoccurrence of the unwanted sludge deposits by devising the right corrective procedures.

Following to the research conducted by Sitepu *et al*[5], to achieve a fine particle size the very tiny crystalline materials were manually and homogenously ground by an agate mortar and a pestle for 10 minutes, and mounted these fine specimens into the XRD sample holders by front pressing. Subsequently, high-resolution powder XRD data were measured using the Rigaku ULTIMA-IV X-ray powder diffractometer with a copper X-ray tube[1,2,3]. The 2θ Bragg angles were scanned from 4° to 75°. Following to Sitepu et al. (2005), the step size of 0.04° was used. In this study, the total counting time for each data was 71 minutes. Moreover, the measured data were then accurately and quickly identified. Furthermore,

Rietveld refinement of all XRD data sets was accurately and precisely used to determinethe weight percentage (wt%) for each of the identified phases. The results are given below in turn.

## RESULTS AND DISCUSSIONS

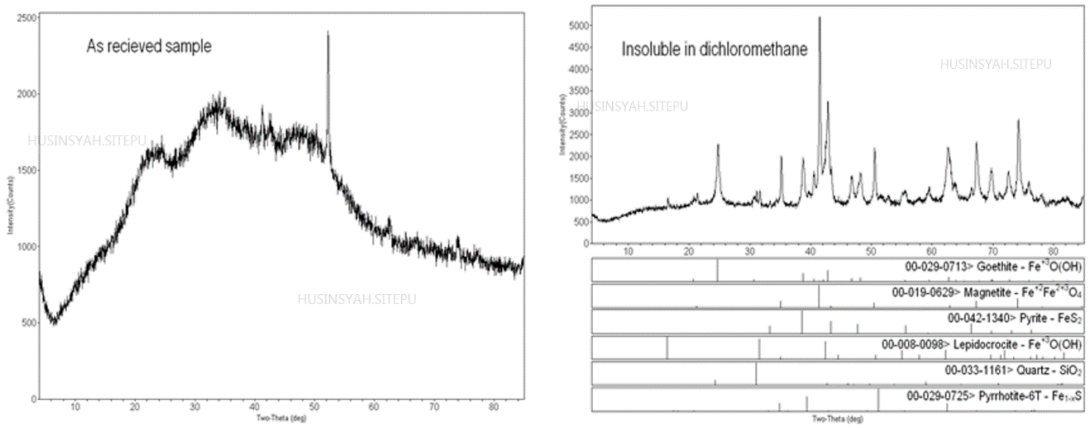
### Very Small Quantities of the Crystalline Deposits Collected from Refinery

The measured XRD pattern of the as-received deposits mainly consists of the non-crystalline materials or amorphous, see Figure 1(a). Noted, that, this type of XRD pattern unfortunately cannot be identified, because phase identification relies on the three-strongest peaks of XRD data of crystalline materials. Therefore, the crystalline deposits part must be separated from the amorphous (hydrocarbon part) of the as-received sludge deposits. When the crystalline deposits part separated from the non-crystalline materials (hydrocarbon part), the XRD pattern of the very small quantities of the inorganic deposits part shows crystalline materials, see figure 1(b). Subsequently, the measured XRD data of the tiny crystalline deposits part were then identified by X'Pert High Score plus Version 4.3. PANalytical Inc. Here, the International Powder Diffraction Data (ICDD, 2018)[14] of the powder diffraction file (PDF-4+) database of the standard reference materials was used to perform qualitative analysis (finger prints or phase identification). The results revealed that the XRD data of the very small quantities of the inorganic deposits part consisted of (i) three types of iron oxide corrosion products with different crystal structure ─ goethite with the chemical formula of FeO(OH), magnetite with the chemical formula of $Fe_3O_4$ and lepidocrocite with the chemical formula of FeO(OH), (ii) two types of iron sulfide corrosion products with different crystal structure systems ─ pyrite with the chemical formula of $FeS_2$ and pyrrhotite with the chemical formula of $Fe_7S_8$, and (iii) quartz with the chemical formula of $SiO_2$, see figures 1(b).

When all the phases were identified (i.e., finger prints or qualitative analysis), the next step was to precisely determine the contents for each of the phases (i.e., quantitative phase analysis) by Rietveld method where whole powder patterns were included in the refinement. The results revealed that the XRD data of the very small quantities of the crystalline deposits part mainly consisted of 82.0 wt% of three types of iron oxide corrosion products with different crystal structures. They are 56.0 wt% of goethite with the chemical formula of FeO(OH), 15.0 wt% of magnetite with the chemical formula of $Fe_3O_4$ and 11.0 wt% of lepidocrocite with the chemical formula of FeO(OH). The additional 18.0 wt% of others materials are 16.0 wt% of iron sulfide corrosion products and 2.0 wt% of formation material, see Figure 2.

The relationship between the Rietveld quantitative phase analysis of XRD of the tiny crystalline deposits part, and corrosion deposits nature at ambient pressure and high temperature can be briefly described as,

- Magnetite iron oxide corrosion products coat the iron to avoid oxygen and reach underlying metal. Moreover, at ambient pressure and low temperature, the mostly accumulated lepidocrocite iron oxide corrosion product transformed into most stable goethite iron oxide corrosion product; and
- Pyrrhotite iron sulfide corrosion products results from the sulfur corrosive action not only on the iron, but also due to the moisture.




(a) **Amorphous as-Received Deposits.** **(b) Crystalline Inorganic Deposits Part.**

**Figure 1. (a) The Measured XRD Pattern of the As-Received Deposits Collected from the particular Failure Equipment in a Refinery. (b) Qualitative Analysis Results (Finger Prints or Qualitative Analysis) of the Very Tiny Crystalline Deposits Part.**

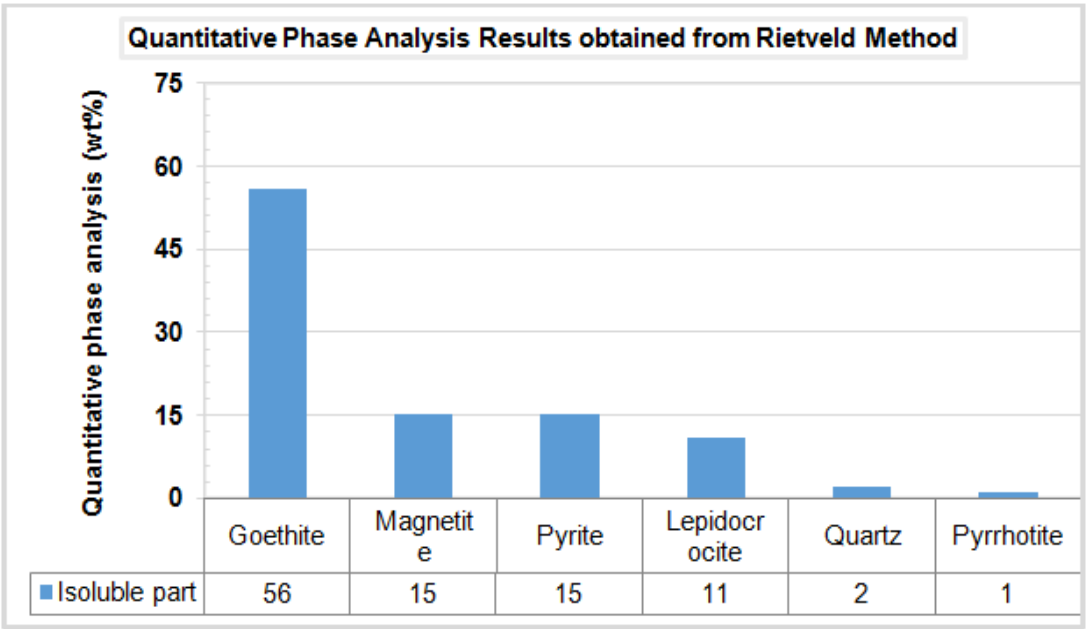
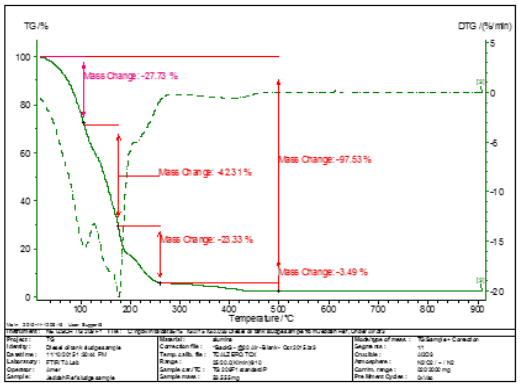
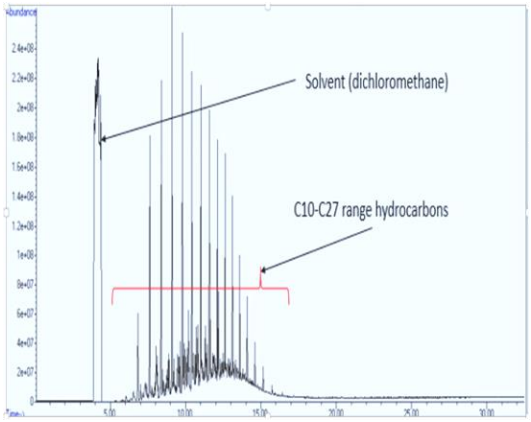



**Figure 2. Quantitative Phase Analysis Results (wt%) for each of the Identified Phases Obtained from Rietveld Refinement with the March Model from Preferred Orientation Correction.**

Figure 3(a) shows the results obtained from spectrometry thermal gravimetric analysis (TGA), which shows 72.0 wt% of hydrocarbon part, 25.0 wt% of water and 3.0 wt% of crystalline materials part of deposits. When the 72.0 wt% of hydrocarbon part was analyzed by gas chromatography mass spectrometry (GC-MS), it was found that the range of carbon is from C10 to C27, see figure 3(b). The findings suggest that diesel is the type of hydrocarbon part deposits. Knowing which crystalline phases/compound sand type of non-crystalline materials (amorphous or hydrocarbon part) that presents at the deposits from the specific affected equipment in a refinery can guide the engineers to overcome the problems by devising right corrective actions.




**(a) Spectroscopy TGA Results.**




**(b) Spectrometry – GCMS Results.**

**Figure 3. (A) The Spectrometry TGA Analysis yielded 72.0 wt% of Hydrocarbon part, 25.0 wt% of Water and 3.0 wt% of Crystalline Deposits. (B) Spectrometry GCMS Analysis of the 72.0 wt% of Hydrocarbon part Showed C10 to C27 Carbon range, Suggesting that Diesel is the type of Hydrocarbon part Deposits.**

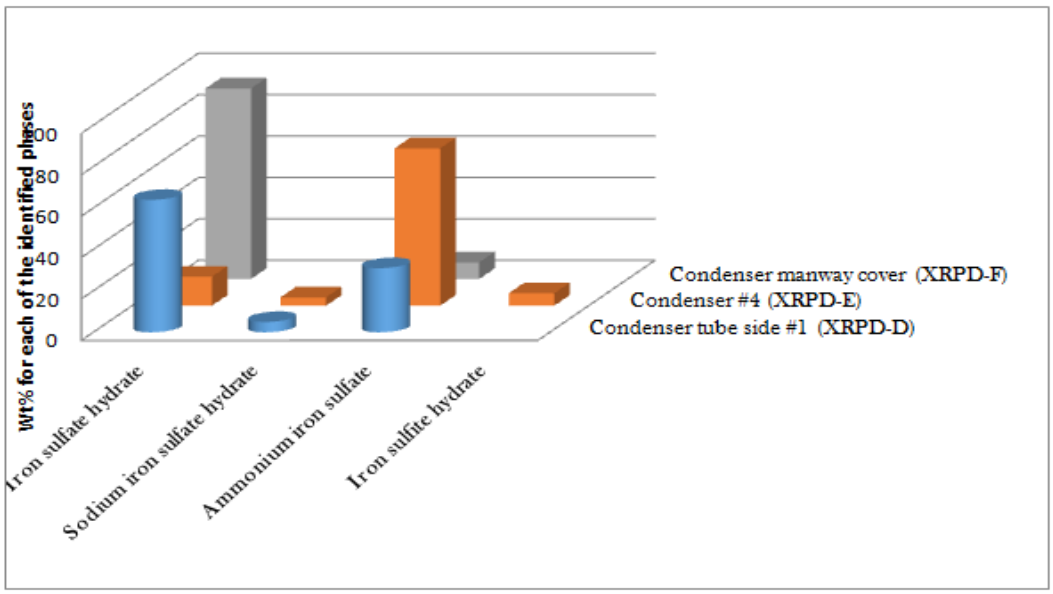



**Figure 4. Wt% for each of the Identified Phases Obtained from Rietveld Refinement with the March Model for Preferred Orientation Correction for all XRD Data sets of Crystalline Deposits part Collected from the Particular Failure Equipment in Sulfur Recovery Unit.**

### Very Tiny Crystalline Deposits Part Collected from Equipment at Sulfur Recovery Unit

The accumulated deposits inside the particular failure equipment in sulfur recovery unit usually can cause operational problems. Therefore, the authors provide the solutions by accurately and quickly identifying the XRD data of the crystalline deposits by High Score Plus software. If all the phases/compounds are identified correctly (qualitative analysis), the contents for each of the identified phase can be determined precisely by Rietveld method. The challenges in this study were to determine quickly, accurately and precisely the quantitative phase analysis (wt%) for each of the identified phases by Rietveld method of the tiny crystalline deposits part.

One of the authors (Husin Sitepu) has continuously conducted research on structural, texture and phase composition of the X-ray, synchrotron and neutron powder diffraction data of crystalline materials (Sitepu et al., 2005; Sitepu, 2009) and extended the work to overcome the challenges in this study since 1989. The X-ray crystallography results revealed that the crystalline deposits part mainly consist of iron sulfate corrosion product which agreed with the results obtained from the other locations at different refineries and gas plants[1,2,3]. Additionally, some sodium and ammonium iron sulfate corrosion products were also detected, see figure 4.

For deposits that were collected from condenser tube side and condenser man way cover, the major phase is an iron sulfate corrosion product. The compound - ammonium sulfate - is the major phase obtained from the Rietveld method for the crystalline deposits from condenser. Additionally, the compound - sodium iron sulfate – detected as the minor phase in both condenser tube side and condenser. The compound - iron sulfite phase – is appeared in condenser; however, this type of compound was undetected in condenser. Noted that, both compounds – iron sulfate hydroxide and ammonium iron sulfate hydroxide - are the trace materials found in condenser tube side and condenser man way cover, respectively. The results agreed well with the previous study from different failure equipments[1,2,3].

It can be summarized from the present study that the combined methods and refinements developed by Sitepu and Zaidi (2017)[3] and Sitepu et al (2005) and Sitepu (2009)[15] have been extended to quickly, precisely and accurately (i) separate the crystalline deposits part from the non-crystalline materials (amorphous or hydrocarbon part) of the as-received sludge deposits build up in the specifics affected system in the field, and (ii) determine the quantitative Rietveld phase phases of XRD data of very tiny amount of crystalline specimens. The authors conducted the above challenges work to determine quickly, accurately and precisely the weigh percentage (wt%) or quantitative phase analysis of the crystalline deposits part mainly because the research findings guide the engineers to take preventive action and avoid the particular failure equipment.

## CONCLUSIONS

Based on the quantitative phase results obtained from Rietveld refinement with the March model for preferred orientation correction, it can be concluded that:

- The chemical compounds - iron oxide corrosion products with the mineral name of goethite and chemical formulae of FeO(OH) mainly appeared at the very tiny amount of crystalline deposits part collected from the refinery. It suggests that at low temperature the mostly formed phase is lepidocrocide with the chemical formula of FeO(OH) and with time it transformed into the most stable goethite phase.
- The chemical compound – iron oxide corrosion products mainly appeared at the very small quantities of the crystalline part deposits collected from the steam drum of the process equipment of sulfur recovery unit. Additionally, iron sulfate corrosion products mainly appeared at the very small quantities of the crystalline non-hydrocarbon part deposits in the condenser.
- The research findings, which are supported by XRF results, guide the field engineers and scientists to draw up the right procedures and take preventive action in overcoming the particular failure equipment.

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