

## QUANTITATIVE PHASE ANALYSIS OF XRD DATA OF SLUDGE DEPOSITS FROM REFINERIES AND GAS PLANTS BY USE OF THE RIETVELD METHOD

Husin Sitepu and Rasha A. Al-Ghamdi

Research & Development Center, Saudi Aramco, P.O. Box 62, Dhahran, Saudi Arabia

### ABSTRACT

In this paper, structural, texture and phase composition of the X-ray powder diffraction (XRD) data — generated from scale and corrosion deposits from boiler equipment at a gas plant — was conducted using the Rietveld method, with the generalized spherical harmonics description for preferred orientation correction [Sitepu (2009). *Powder Diff.*, **24**, 315-326]. Subsequently, the sample preparation methods— developed by the authors — to separate the inorganic materials from the hydrocarbon of the sludge deposits and the other materials, were extended to perform quantitative phase analysis of XRD data, generated from deposits collected from: the external surface of the boiler tubes in a refinery, the inside screen cutout and the inside section of the boiler tube in a refinery, the screen tube of a boiler and condenser at a gas plant, and a condenser at a gas plant. The results revealed good agreement between the measured and calculated XRD patterns of scale deposits, in the form of calcium carbonate (calcite- $\text{CaCO}_3$ ) formed on the boiler equipment at a gas plant; when the generalized spherical harmonics description was used to correct the intensities due to the effects of preferred orientation, and the refined structural parameters agreed well with the XRD single crystal. Therefore, the findings suggest that the fuel is poor if the vanadium oxide ( $\text{V}_2\text{O}_5$ ), sodium vanadium oxide ( $\text{NaV}_2\text{O}_5$ ) and sodium vanadium sulfate hydrate ( $\text{Na}_2\text{V}(\text{SO}_4)_2$ ) phases appear in the examined ash deposits. Furthermore, the boiler feed water contains dissolved oxygen — if the corrosion product is in the form of hematite ( $\text{Fe}_2\text{O}_3$ ) and is present in the boiler deposits. Moreover, the presence of metallic copper in the deposits suggests erosion in the boiler tubes. Therefore precautions must be taken to prevent the plating out of copper during cleaning operations.

### INTRODUCTION

The sludge deposits that frequently accumulate inside oil industry equipment can cause failures and temporarily shut down operations. Sitepu, et al. (2018; and referenced in) described the new methods in sample preparation to identify the accumulated deposits from refineries and gas plants, and assessed these methods for each of the as-received sludge samples. These methods include:

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

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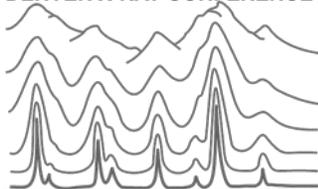
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2. For the unknown materials produced with sulfur product, deposits must be analyzed without pretreatment.
3. For oil-based sludge, it was treated with dichloromethane and then filtered in the filtration assembly, and therefore, the (i) dichloromethane insoluble part (i.e., inorganic materials or non-hydrocarbon) was investigated by X-ray powder diffraction (XRD) data and the Rietveld method, and (ii) the dichloromethane soluble part (i.e., hydrocarbon) was analyzed by gas chromatography mass spectrometry (GCMS).

Sitepu, et al. (2018; and referenced in), and Al-Ghamdi and Sitepu (2018) indicated that the XRD data of a small amount of the unknown inorganic materials were successfully and accurately identified. Sitepu, et al. (2018; and referenced in), and Al-Ghamdi and Sitepu (2018) pointed out that the method is quick and can accurately identify very small quantities of inorganic materials present in the sludge deposits. Moreover, they refined all of the XRD data of the identified phases by using the Rietveld method quantitatively, and then calculated the weight percentage (wt%) for each of the identified phases. When all the phases of XRD data of the inorganic materials' part are identified accurately, Sitepu, et al. (2018; and referenced in) subsequently used the Rietveld method, which adjusts the refinable parameters until the best fit of the entire calculated pattern to the entire measured XRD pattern is achieved, to determine the phase composition (or wt%),  $W_p$ , (i.e., quantitative phase analysis) for each of these identified phases:  $p$ , is proportional to the product of the scale factor,  $s$ , as derived in the Rietveld phase analysis, with the mass and volume of the unit cell, and is given by:

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

where  $Z$ ,  $M$ , and  $V$  are the number of formula units per unit cell, the mass of the formula unit, and the unit-cell volume (in  $\text{\AA}^3$ ), respectively [Bish and Howard, 1998; Hill, 1991; Hill and Howard, 1987; O'Connor and Raven, 1988]. The advantages of the Rietveld method are:

- The calibration constants are computed from simple literature data (i.e.,  $Z$ ,  $M$ , and  $V$  values) rather than by laborious experimentation.
- All reflections in the pattern are explicitly included, irrespective of overlap.
- The background is better defined since a continuous function is fitted to the whole powder diffraction pattern.
- The preferred orientation effects can be corrected and determined [Sitepu, et al., 2005; Sitepu, 2009 and referenced in].
- The crystal structural and peak profile parameter scan can be refined as part of the same analysis.

In this paper, the method developed by Sitepu and Zaidi (2017) and Sitepu, et al. (2018) was extended to the deposits collected from the boiler equipment, which consists of a furnace, boiler tubes, steam drum, mud drum, and the boiler, and therefore when the furnace produces heat for

the boiler, the water in it changes into steam. The failure of boiler tubes mainly occurred due to the accumulated deposits in the equipment in refineries and gas plants, and ultimately slowed down the production. Therefore, the field engineers requested the authors to identify the nature and source of the XRD data of deposits by using the High Score Plus software (X'Pert High Score Plus Version 3.0e PANalytical Inc.) (Degen, et al., 2014), combined with the International Powder Diffraction Data (ICDD, 2018) of the powder diffraction file (PDF-4+) database of the standard reference materials. Additionally, the authors provide the findings and support to the plant engineers, to take proper action to prevent future occurrences, thereby avoiding a plant slowdown that could result in loss of production.

The main objective of the present study was to extend the new method developed by Sitepu, et al. (2018; and referenced in), to particularly and accurately examine the phase identification of inorganic materials (non-soluble or non-hydrocarbon) — found in different pieces of equipment at refineries and gas plants. Additionally, the authors determined the nature, source and formation mechanism of deposits formed in the boilers of refineries and gas plants. Once all the phases for each of the unknown inorganic deposits' XRD data had successfully been identified, then the quantitative phase analysis of XRD data for each phase was determined using the Rietveld method with the generalized spherical harmonic description [Sitepu, et al., 2005; Sitepu, 2009 and referenced in]. The findings will help refinery and gas plant employees take proper action to prevent future occurrences.

## EXPERIMENTAL PROCEDURE

The method of sample preparation procedures — developed by the authors — was extended to characterize the inorganic materials present in the sludge deposit samples, received from many different equipment items, located in refineries and gas plants. A prerequisite is the accurate phase identification and quantification results of inorganic materials or the insoluble parts. The phase composition is required to facilitate chemical cleaning of the particular failed equipment, and prevent reoccurrence.

The small amount of the inorganic materials (i.e., non-hydrocarbon part) were manually ground by an agate mortar and a pestle for several minutes to achieve a fine particle size, and mounted into the XRD sample holders by front pressing. Subsequently, high-resolution XRD data of the inorganic materials were measured using the Rigaku ULTIMA-IV X-ray powder diffractometer, with a copper X-ray tube, scan range  $10^{\circ}$  to  $120^{\circ}$   $2\theta$ , with a step size of  $0.04^{\circ}$ , and a scan rate of  $1^{\circ}$  per minute. Moreover, all of the XRD data sets of the inorganic materials, which show no amorphous inorganic phases present of inorganic deposits, were then identified by High Score Plus software combined with the ICDD PDF-4+ database of the standard reference materials. The Rietveld method was used to accurately determine the phase composition (wt%) for each of the identified phases according to equation (1).

## RESULTS AND DISCUSSIONS

### A. Crystal structures and preferred orientations refinement of XRD data of carbonate scale deposits in the form of calcium carbonate from a gas plant

The refined structural parameters obtained from the Rietveld refinement agreed well with the single-crystal XRD data results and powder XRD results for calcite [ $\text{CaCO}_3$ ]. The space group used was R-3c (No. 167). Wyckoff coordinates: 6(c) are 0,0,0, and 0,0,  $\frac{1}{2}$ ; 6(a) are 0,0,  $\frac{3}{4}$ ; and 18(e) are x,0, $\frac{1}{4}$ ; -x,-x,  $\frac{1}{4}$ ;-x,0,  $\frac{3}{4}$ ;0,-x,  $\frac{3}{4}$ , and x,x,  $\frac{3}{4}$ . Cell formula unit Z=6 and formula weight =100.09.

Table 1 depicts the unit-cell parameters of the carbonate scale, in the form of calcium carbonate [calcite- $\text{CaCO}_3$ ], obtained from the Rietveld refinement with the generalized spherical harmonics description. The number parentheses give the estimated standard uncertainty for the least significant figure of the parameter. The refined structural parameters (Table 2), except the isotropic temperature factor, agreed well with the corresponding single-crystal XRD results for calcite [ $\text{CaCO}_3$ ] [Maslen, et al., 1995]. Therefore the generalized spherical harmonics description is recommended for the preferred orientation correction in XRD analysis, for both crystal structure refinement and phase composition analysis.

Figure 1 shows the agreement between the calculated and measured XRD pattern for the carbonate scale, in the form of calcium carbonate [calcite- $\text{CaCO}_3$ ], following Rietveld refinement with the generalized spherical harmonic description. Figure 2 shows the plots of the pole density distribution function, with an orientation angle derived from the Rietveld refinement with the generalized spherical harmonic description, where the pole density distribution function for <104> calcite data was derived from the Rietveld refinement. In the case of an ideal random orientation, the pole density distribution function is unity, Figure 2. As expected for the XRD data for the carbonate scale deposits with the refined texture index,  $J=1.0854(7)$ , which is not randomly oriented, the pole density distribution function is maximum at the orientation angle  $\varphi = 0^\circ$  and minimum at  $\varphi = 90^\circ$ . The crystallographic figures-of-merit ( $R_P$ ,  $R_{WP}$ ,  $R(F^2)$ ), and goodness-of-fit index ( $\chi^2$ ) obtained from the Rietveld refinement, with the generalized spherical harmonic description, are  $R_P = 9.75$ ,  $R_{WP} = 13.30$ ,  $R(F^2) = 10.15$ ,  $\chi^2 = 1.32$ ; and the texture index is 1.0854(7).

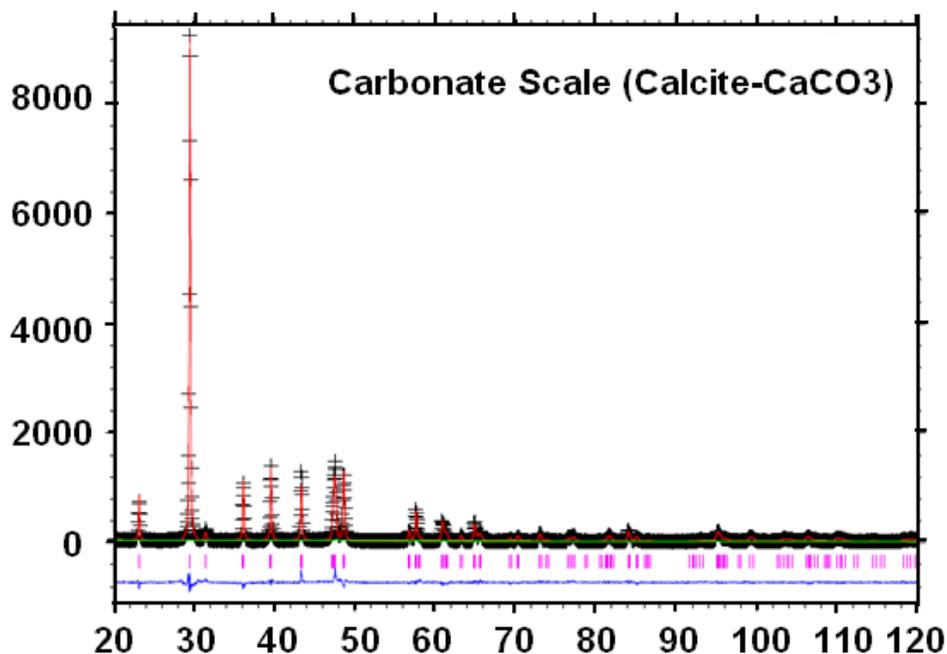
Knowing accurately which phases and concentrations were involved in the deposits, can guide the field engineers at the refinery and gas plants to facilitate efficient cleaning of the effected equipment by drawing up the right procedures and taking preventive action to stop the generation of those particular deposits.

**Table 1.** Summary of the refined cell parameters of carbonate scale in the form of  $\text{CaCO}_3$  obtained from the Rietveld refinement with a generalized spherical harmonics description for preferred orientation correction. The reference cell parameters are included.

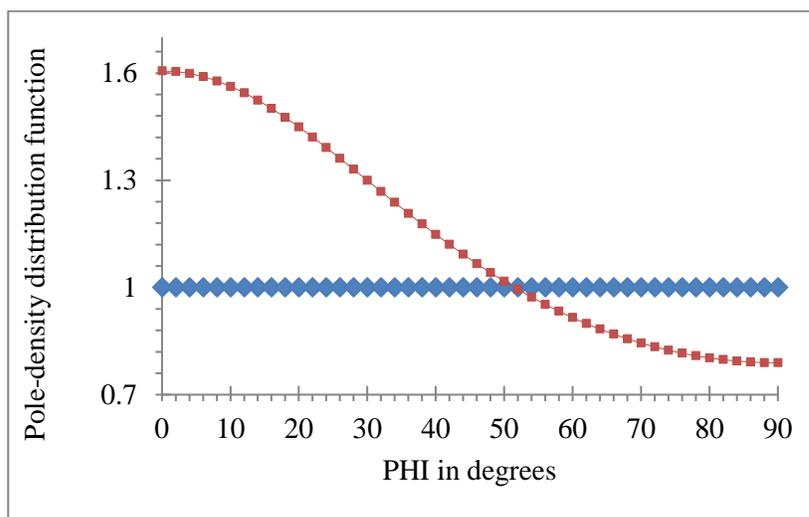
Para- meters	This Study	Maslen, et al.(1995)	Sitepu, et al. (2005)	Markgraf & Reeder	Antao, et al. (2008)	Balirano
a (Å)	4.97630(15)	4.988(2)	4.991(1)	4.988(1)	4.9877648(1)	4.98879(7)
c (Å)	17.0904(9)	17.068(2)	17.068(2)	17.061(1)	17.05242(2)	17.0649(4)
V (Å) <sup>3</sup>	366.520(31)	367.8(3)	368.204(2)	367.6(1)	367.3911(4)	367.81(1)

**Table 2.** Summary of the refined atomic positions of carbonate scale in the form of  $\text{CaCO}_3$ , obtained from Rietveld refinement with the generalized spherical harmonics description model.

Atomic Positions	This Study	Maslen, et al. (1995)	Sitepu (2005)	Markgraf& Reeder	Antao, et al. (2008)	Balirano
<b><i>Atomic Positions &amp; Anisotropic Displacement Coefficients</i></b>						
<b>Ca(0,0,0)</b>						
U <sub>iso</sub>	0.0162(5)	0.00988(3)	0.232(2)	0.94(3)	0.80(4)	1.203(4)
<b>C(0,0,¼)</b>						
U <sub>iso</sub>	0.0110(16)	0.00834(9)	0.232(2)	0.93(5)	0.76(6)	1.644(2)
<b>O(x,0,¼)</b>						
x	0.2544(4)	0.25700(6)	0.257(9)	0.2567(2)	0.250(1)	0.2564(9)
U <sub>iso</sub>	0.0247(9)	0.1129(7)	0.309(8)	1.51(4)	1.44(6)	1.644(2)
<b><i>Bond Length</i></b>						
Ca-O			2.379(1)	2.3595(5)	2.3574(2)	2.3608(7)
C-O			1.248(2)	1.280(1)	1.2836(3)	1.279(1)
<b><i>Figures-of-Merit and Goodness-of-Fit Index</i></b>						
R <sub>P</sub>	9.75					
R <sub>WP</sub>	13.30					
R(F <sup>2</sup> )	10.15					
χ <sup>2</sup>	1.32					
J	1.0854(7)					



**Figure 1.** The agreement between the calculated and measured XRD patterns for the carbonate scale deposits following the Rietveld refinement, with the generalized spherical harmonics description for preferred orientation correction.



(b)

**Figure 2.** The variation between the pole density distribution function with the orientation angle. The pole density distribution function for  $\langle 104 \rangle$  calcite data is derived from the Rietveld refinement.

### **B. Quantitative phase analysis of XRD data by Rietveld method for ash deposits collected from an external surface of the boiler tubes in a refinery**

The phase identification of the XRD data, which show no amorphous inorganic phases present of inorganic deposits, was conducted to determine the source and formation mechanism, and therefore the phase composition for each of the identified phase results can be used by the engineers to take corrective measure, prevent scale build up and avoid future tube failure.

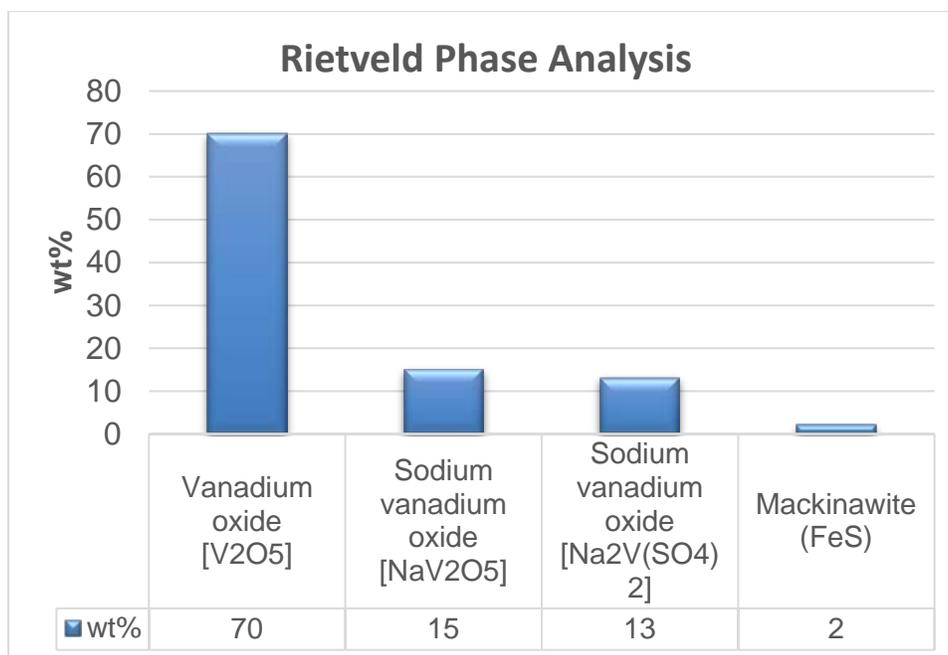
Figure 3 shows the phase composition of the identified results obtained from the Rietveld refinement for each of the identified phases of XRD data of ash deposits from the external surface of the boiler tubes in a refinery, where the refinery boiler is an oil fired boiler. The quantitative phase analysis results showed the phase composition was found to be 70 wt% of vanadium oxide ( $V_2O_5$ ), 15 wt% of sodium vanadium oxide [ $NaV_2O_5$ ], 13 wt% of sodium vanadium sulfate hydrate [ $Na_2V(SO_4)_2 \cdot H_2O$ ], and 2 wt% mackinawite ( $FeS$ ) compounds.

The findings suggest that when fuel oil is burned, approximately all of the vanadium and sodium compounds present in the fuel — in high quantities — react with oxygen to form  $V_2O_5$  and  $Na_2O$  in the furnace and stick to the metal surface. When formed the two compounds react on the metal surface, it forming a low melting phase — sodium vanadate. Under optimum conditions, both  $V_2O_5$  and  $Na_2O$  can form a liquid flux that can protect the oxide scale, exposing the underlying metal to oxidation, and therefore, the ash deposits built up in the boiler tubes in a refinery pose potential corrosion problems. Additionally, when the  $NaV_2O_5$  appeared in the ash deposits in the boiler tubes of a refinery, fuel-ash corrosion occurred. Fuel oils contain low quantities of vanadium, where sodium and sulphur was used to mitigate fuel-ash corrosion. The other options to prevent the formation of a low melting point phase of the sodium vanadate complexes is by adopting a fuel additive treatment.

### **C. Quantitative phase analysis of XRD data by Rietveld method for scale deposits collected from the inside screen of a section cut-out and inside a large boiler tube in a refinery**

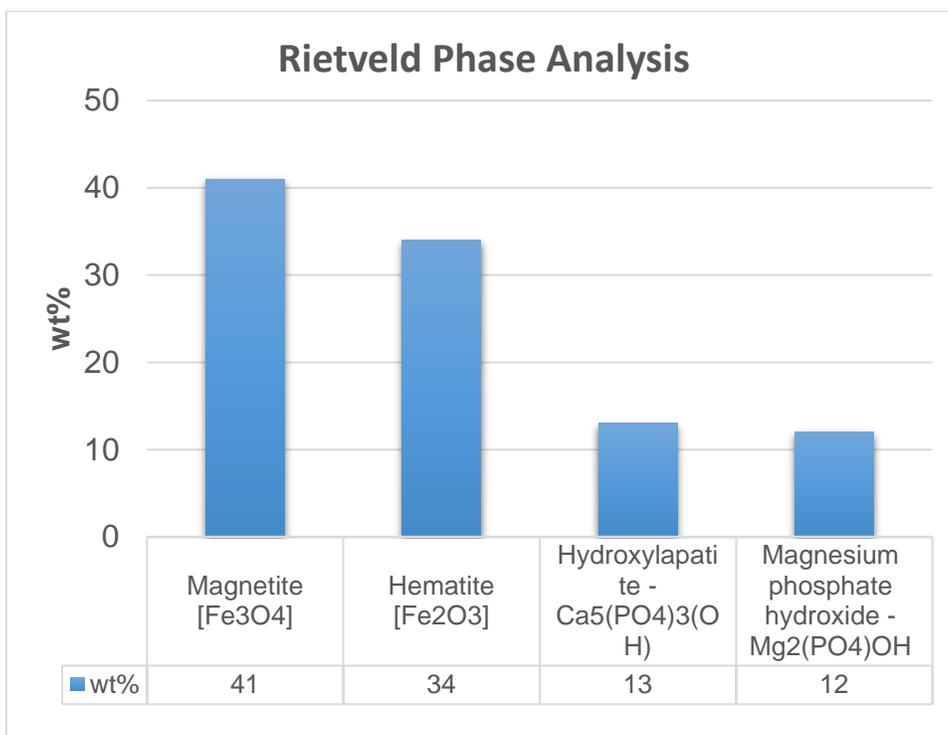
The phase composition analysis of the scale deposits from the inside screen of a section cutout and inside a large boiler tube from a refinery, which were observed in high-pressure boiler tubes at the refinery, was required to identify the deposits present inside of the tube. The identification of the deposits helped to design a procedure for chemical cleaning without damaging the boiler tubes.

Figure 4 shows the Rietveld phase analysis of the scale deposits scraped from the insides of the tubes, which mainly consisted of 75 wt% of iron oxide corrosion products, in the form of 41 wt% magnetite ( $Fe_3O_4$ ) and 34 wt% hematite ( $Fe_2O_3$ ), with the additional phases being 13 wt% of calcium phosphate hydroxide (apatite), and 12 wt% of magnesium phosphate hydroxide for the

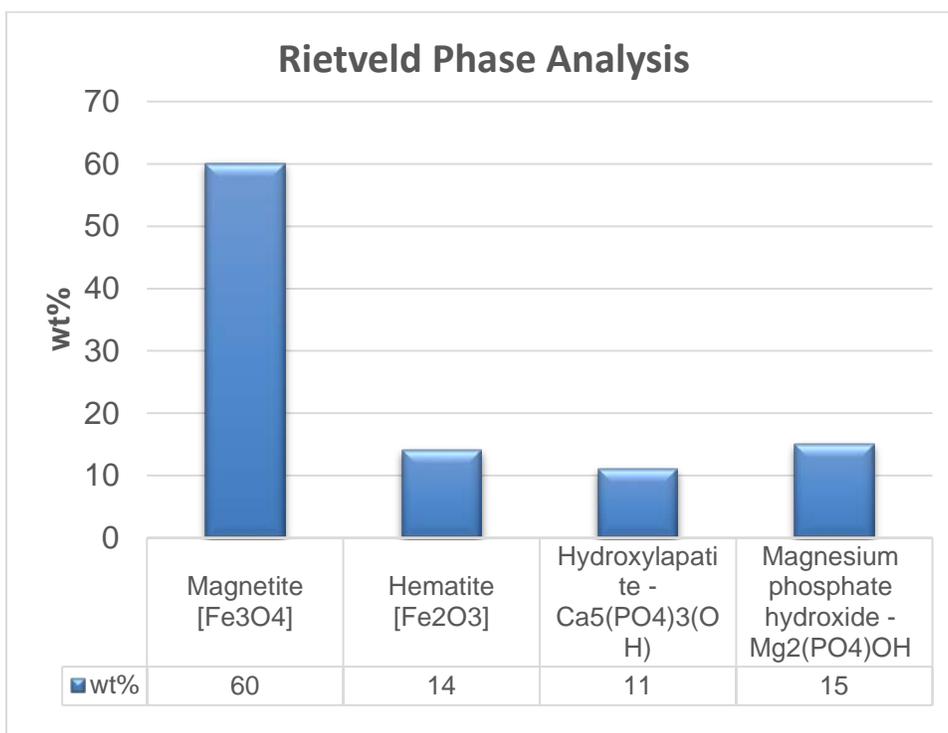


**Figure 3.** Rietveld phase analysis of XRD data of ash deposits collected from the external surface of the boiler tubes in the refinery.

scale deposits from the inside screen of the section cutout. Additionally, the phase composition analysis of the scale deposits from inside a large boiler tube from a refinery, revealed 74 wt% of iron oxide corrosion products, in the form of 60 wt% of magnetite (Fe<sub>3</sub>O<sub>4</sub>) and 14 wt% of hematite (Fe<sub>2</sub>O<sub>3</sub>), with the additional phases being 11 wt% of calcium phosphate hydroxide (apatite), and 15 wt% of magnesium phosphate hydroxide. Note that iron oxide corrosion products in the form of 34 wt% of Fe<sub>2</sub>O<sub>3</sub> for scale deposits from inside a large boiler tube, and 14 wt% of Fe<sub>2</sub>O<sub>3</sub> for the scale deposits from inside a large boiler tube, suggest the presence of dissolved oxygen in the boiler water.



**(a)** Inside the screen of a section cutout

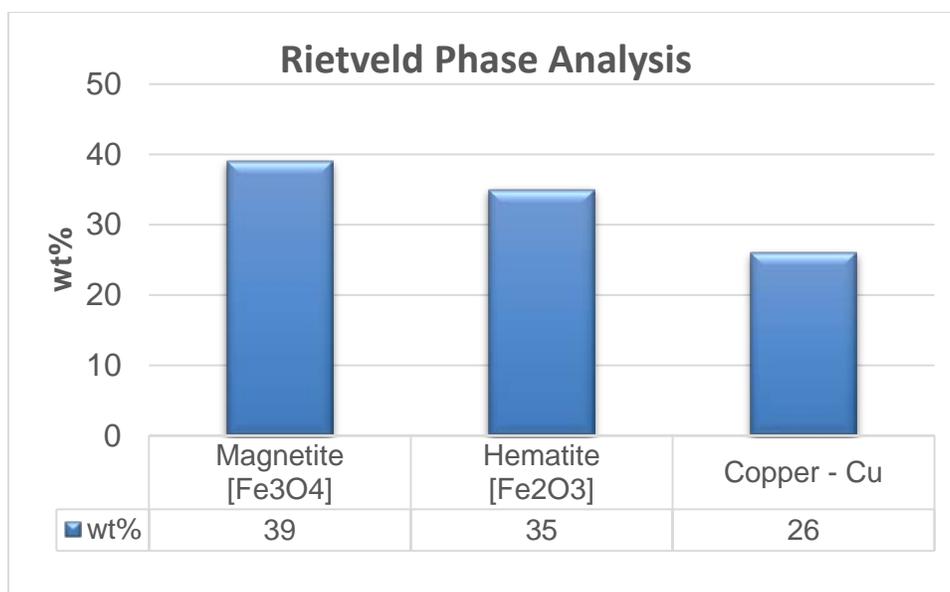


**(b)** Inside a large boiler tube from a refinery

**Figure 4.** Rietveld phase analysis results of the scale deposits from **(a)** inside the screen of a section cutout, and **(b)** inside a large boiler tube from a refinery.

#### D. Quantitative phase analysis of XRD data by Rietveld method for deposits collected from screen tubes of boiler and condenser at a gas plant

The boiler tube failed due to the built up deposits, and therefore phase composition results were required by the field engineers to support their failure analysis work. Figure 5 shows the phase composition results for each of the identified phases obtained from the Rietveld refinement. The Rietveld phase analysis revealed that the deposits from screen tubes of a boiler and a condenser at the gas plant, consisted of 74 wt% iron oxide corrosion products, in the form of magnetite ( $\text{Fe}_3\text{O}_4$ ) and metallic hematite ( $\text{Fe}_2\text{O}_3$ ), with the addition of 26 wt% of Cu. Note that the high wt% of  $\text{Fe}_2\text{O}_3$  and Cu indicate the presence of dissolved oxygen in the boiler feed water, and erosion in the boiler tubes respectively.



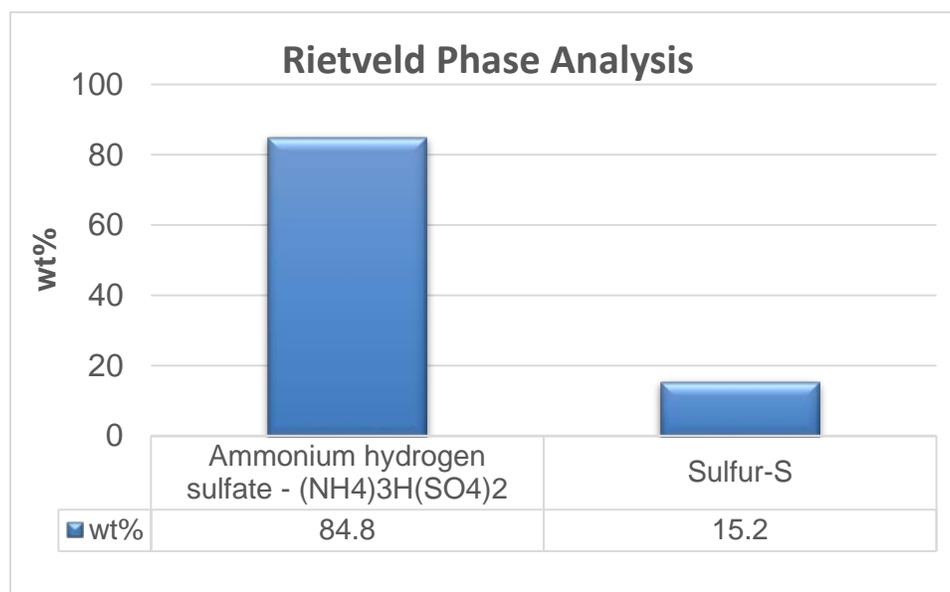
**Figure 5.** Rietveld phase analysis results of the deposits from the screen tubes of a boiler and a condenser at the gas plant.

#### E. Quantitative Phase Analysis of XRD Data by Rietveld Method for Scale Deposits Produced with Sulfur Product from a Condenser at a Gas Plant

The main objective of the deposits investigated by XRD data and the Rietveld method, was to support the field engineers. Note that the field engineers were concerned that the unknown deposits produced with a sulfur product from a condenser at a gas plant might be coming from the alumina and silica of the superclaus catalyst, which is a silica (Si) based extrudate with higher surface area and more active at lower operating temperatures than the alpha-alumina ( $\alpha$ -Al) based catalyst. If the XRD phase identification results showed the deposits consist of alumina and silica, it suggested that the mesh holding the catalyst has a pinhole, and therefore the

catalyst leaks will definitely require total shut down of the gas plant, and repair and remove the catalysts.

Figure 6 shows the Rietveld phase analysis results for each of the identified phases, obtained from the Rietveld refinement of the XRD data of the unknown deposits, were produced with a sulfur product from a condenser at a gas plant. The results revealed that the deposits mainly consisted of 84.8 wt% ammonium hydrogen sulfate  $[(\text{NH}_4)_3\text{H}(\text{SO}_4)_2]$  and 15.2 wt% sulfur (S). The findings show that no alumina nor silica appeared in the deposits, suggesting that the mesh holding the catalyst is good. Due to the treatment with chemical containing ammonia, the  $[(\text{NH}_4)_3\text{H}(\text{SO}_4)_2]$  could be formed in the boiler feed water. The formation of  $[(\text{NH}_4)_3\text{H}(\text{SO}_4)_2]$  can be avoided by increasing the furnace temperature that will burn ammonia.



**Figure 6.** Rietveld phase analysis results of the unknown deposits produced with sulfur product from a condenser at a gas plant.

It can be summarized that phase identification of the XRD data of deposits obtained from the High Score Plus software combined with the PDF-4+ database, and phase composition for each of the identified phases obtained from the Rietveld refinement are excellent tools to determine the nature, source, and formation mechanism of deposits formed by the processes in the various units of refineries and gas plants. Therefore the results guided the engineers at the refineries and gas plants to overcome problems by designing the chemical cleaning procedures that will not damage the equipment and avoid future equipment failure.

## CONCLUSIONS

Based on the structural, texture and phase composition of the XRD data, which show no amorphous inorganic phases present of inorganic deposits, obtained from the Rietveld method and generalized spherical harmonic description for crystallographic preferred orientation corrections, we found the following:

- Good agreement between the measured and calculated XRD patterns of scale deposits in the form of calcium carbonate (calcite- $\text{CaCO}_3$ ) from boiler equipment at a gas plant; and the refined structural parameters except the isotropic temperature factor agreed well with the XRD single crystal data.
- Rietveld phase analysis yields the results for the deposits built up in the affected equipment at the refinery and gas plants, and therefore, the findings suggest that the fuel is poor if the vanadium oxide ( $\text{V}_2\text{O}_5$ ), sodium vanadium oxide ( $\text{NaV}_2\text{O}_5$ ), and sodium vanadium sulfate hydrate ( $\text{Na}_2\text{V}(\text{SO}_4)_2$ ). Furthermore, the boiler feedwater contains dissolved oxygen, if the corrosion product in the form of hematite ( $\text{Fe}_2\text{O}_3$ ) is present in the boiler deposits.
- The presence of metallic copper in the deposits suggests erosion in the boiler tubes, and therefore precautions must be taken to prevent the plating out of copper during cleaning operations.
- Knowing accurate quantitative analysis results for each phase involved in the scale deposits, facilitates chemical cleaning and prevents reoccurrence by stopping the generation of those particular deposits.

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