

QUANTITATIVE RIETVELD PHASE ANALYSIS OF SCALE AND CORROSION PRODUCTS FORMED INSIDE OIL AND GAS INDUSTRY EQUIPMENT: AN IMPORTANT INDUSTRIAL CHALLENGE

Husin Sitepu & Rasha A. Al-Ghamdi

Research and Development Center, Saudi Aramco, Dhahran, Saudi Arabia

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ABSTRACT

Scale and corrosion deposits — that accumulate inside oil industry equipment — can cause failures and temporarily shut down refineries and gas plants. Recently, Sitepu and Al-Ghamdi (2019); and Al-Ghamdi and Sitepu (2018) described a new method to separate the nonhydrocarbon part (i.e., crystalline inorganic materials) from the hydrocarbon part (i.e., dichloromethane soluble) of the sludge deposits. Also, they quickly and accurately identified the phase identification of X-ray powder diffraction (XRD) data of small amounts of crystalline inorganic materials and performed quantitative Rietveld Phase Analysis for each of the identified phases. The method is fast and can accurately identify very small quantities of inorganic materials present in the sludge deposits.

This paper reports the application of the quantitative Rietveld phase analysis of corrosion and scale products which is certainly an important and industrial application, and a challenge educational paper on the analysis of such deposits is worthwhile. The basic premise of this paper — that preferred orientation can affect the results of quantitative analysis — is important, and worth discussing. Examples of quantitative Rietveld phase analysis of (i) synthetic mixtures of drilling mud in the form of barium sulfate with the mineral name barite (BaSO_4), formation material in the form of silicon oxide mineral name quartz (SiO_2) and iron oxide mineral name hematite (Fe_2O_3); (ii) the unknown natural corrosion products from the high-pressure boiler condensate storage and feed water deaerator; and (iii) structure and texture characterization of calcium carbonate scale in the form of calcite (CaCO_3). Key information is quantitative Rietveld phase analysis, the lattice parameters (which can reflect composition) and information derived from the XRD profile parameters and the preferred crystallographic orientation. All aspects of the microstructure are worth discussing. Iron oxide in the forms of magnetite, goethite, hematite, and lepidocrocite are especially prone to preferred orientation, and so would be worth including in the samples discussed. The quantitative Rietveld phase analysis for all of the XRD data sets revealed that the findings can quickly and accurately guide the field engineers at the refinery and gas plants, to facilitate efficient cleaning of the equipment by drawing up the right procedures, and take preventive action to stop the generation of those particular sludge deposits.

KEYWORDS: *Quantitative Rietveld Phase Analysis, Structural and Texture Refinement, Scale and Corrosion Deposits*

INTRODUCTION

The corrosion deposits are generated in the high-pressure boiler tube equipment in refineries and gas plants and can cause major operational problems, causing a temporary shutdown of the refinery and gas plants¹. Therefore, the authors sought to accurately and quickly investigate the failure of equipment due to the specific carbonate scale and/or corrosion deposits, and provide support to the engineers at the refinery and gas plant by first identifying the nature and source of the phases of deposits being accumulated².

For example, the nature of the:

- Carbonate scale deposit (i.e., calcium carbonate in the form of calcite and aragonite, and iron carbonate in the form of siderite).
- Corrosion products are: (a) at high-temperature magnetite (Fe_3O_4) corrosion product, it will coated the iron/steel to prevent oxygen from reaching the underlying metal, and (b) at low temperature, mostly lepidocrocite formed, and with time it transformed into the most stable goethite (FeOOH), and (c) akaganeite (FeOOH) formed in marine environments. Additionally, the other corrosion product types (greigite- Fe_3S_4 , pyrite- FeS_2 , marcasite- FeS_2 , mackinawite- $\text{FeS}_{0.9}$, and pyrrhotite- Fe_7S_8) — are the pyrophoric iron sulfide (pyrrhotite- FeS) results from the corrosive action of sulfur (S) or sulfur compound (H_2S) on the iron (steel) and moisture.
- Formation materials (i.e., formally found in the sandstone or sand).
- Cementing materials (i.e., ettringite- $\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}$) are investigated quickly and accurately by using X-ray powder diffraction (XRD) data².

The accurate phase identification results of the deposits on inorganic materials (non-hydrocarbon) in the form of carbonate scale or corrosion products are vital to facilitate efficient chemical cleaning of the equipment in refineries and gas plants and prevent the future occurrences to stop the generation of deposits^{2,3}.

When analysts, especially those who do not have a strong X-ray crystallography background, perform a quantitative phase analysis⁴⁻⁷ of the identified phases using the Rietveld method⁸⁻¹⁰, they frequently assume that the deposits formed in oil and gas plants are randomly oriented. In practice, all crystalline materials reveal some degree of crystallographic preferred orientation (i.e., the texture of crystalline materials¹⁰⁻¹⁷).

In this paper, when all the phases of XRD data of inorganic crystalline materials of the corrosion and scale deposits are identified accurately 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, the GSAS Rietveld software¹⁹ will then be used to perform the:

- Synthetic mixtures of 95 wt% of barite (BaSO_4), 3.5 wt% of quartz (SiO_2) and 1.5 wt% of hematite (Fe_2O_3), denoted sample B95Q3.5H1.5; and 87 wt% of barite, 10 wt% of quartz and 3 wt% of hematite, denoted sample B87Q10H3;
- Iron oxide corrosion products from the high-pressure boiler condensate storage and feed water deaerator; and

- Calcium carbonate scale in the form of calcite (CaCO₃).

Therefore, this paper reports the application of the Rietveld method to the quantitative analysis of known synthetic mixture and unknown natural corrosion products, which is certainly an important industrial application and an educational paper on the analysis of such deposits is worthwhile. The basic premise of this paper — that preferred orientation can affect the results of quantitative analysis — is important, and worth discussing. Key information is not only just the quantitative phase concentrations but also the lattice parameters (which can reflect composition) and information derived from the profile parameters and the preferred orientation. All microstructure aspects; for example, goethite and lepidocrocite are especially prone to prefer crystallographic orientation and so would be discussed. Obtaining quantitative phase analysis of the crystalline materials of unknown corrosion and scale products accurately and quickly can guide the field engineers to overcome the problems by drawing up the right procedures and taking preventive action to stop the generation of those particular deposits.

In performing the refinement for quantitative analysis⁴⁻⁷, the Rietveld method⁸⁻¹⁰, which adjusts the refinable parameters until the best fit of the entire calculated pattern to the entire measured pattern is achieved does not require measurement of calibration data nor the use of an internal standard. Subsequently, the Rietveld method requires the crystallographic information file (e.g., crystal structures) that is close to each of the identified phases. This preferred orientation is fully described by the orientation distribution function, which is a mapping of the probability of each possible grain-orientation with respect to the macroscopic sample frame¹¹⁻¹⁸.

The objective of this paper is to discuss the influence of the different parameters (crystal structure, crystallographic preferred orientation) involved in the Rietveld refinement and describe the most recent quantitative XRD studies on corrosion products.

In the GSAS Rietveld refinement program¹⁹, a mathematical method is developed that calculates an intensity, Y_c , at every point in the pattern,

$$Y_c = \sum_h SKF_h^2 P(\Delta T_h) + Y_b \quad (1)$$

where the first term is the Bragg scattering, containing a scale factor, S , a correction factor, K , a structure factor, F_h , and a profile function, $P(\Delta T_h)$, as determined by the displacement, ΔT_h , of the profile point from the reflection position, and the second term Y_b is the background intensity. The sum is over all profile points in all the scans included in the refinements. Within the K in equation (1) is a term that describes the change in intensity for a Bragg reflection due to texture¹¹⁻¹⁸.

Quantitative Rietveld Phase Analysis of Crystalline Materials

The advantages of the Rietveld methods for quantitative phase analysis⁴⁻⁷ of the XRD data of the many identified phases or mixtures are: (a) the calibration constants are computed from simple literature data (i.e., Z , M , and V values) rather than by laborious experimentation, (b) all reflections in the pattern are explicitly included, irrespective of overlap, (c) the background is better defined since a continuous function is fitted to the whole powder diffraction pattern, (d) the preferred orientation effects can be corrected and determined, and (e) the crystal structural and peak-profile parameter scan

can be refined as part of the same analysis. Therefore, the Rietveld quantitative analysis⁴⁻⁷ have been used worldwide to determine the wt% for each of the identified phases without the need for laborious experimental calibration procedures. The right starting crystallographic information file (e.g., space group, cell parameters, atomic positions, etc.) of each phase in a mixture is required for this Rietveld quantitative analysis method. The information can be obtained from the International Crystal Structure Data. The weight of a phase in a mixture is proportional to the product of the scale factor, s_p , as derived in a multiphase Rietveld analysis of the XRD pattern (equation 1), with the mass, M , and volume, V , of the unit cell. If all phases are identified and crystalline, the wt%, W , of phase, p , is given by:

$$W_p = s_p (ZMP)_p / \sum_{i=1}^n s_i (ZMV)_i \quad (2)$$

where s , Z , M , and V are the Rietveld scale factor, the number of formula units per unit cell, the mass of the formula unit, and the unit cell volume (in \AA^3), respectively.

In this study, the crystal structure refinement, phase composition (i.e., Rietveld quantitative analysis) and texture for each phase of corrosion products formed in the oil and gas pipeline were determined using the Rietveld program with the March model for preferred crystallographic orientation correction.

EXPERIMENTAL

Sample Preparation

At the present study, the authors investigated the Quantitative Rietveld Phase Analysis of:

- Synthetic mixtures of drilling mud in the form of barium sulfate with the mineral name barite (BaSO_4), formation material in the form of silicon oxide mineral name quartz (SiO_2) and iron oxide mineral name hematite (Fe_2O_3); and the weight percentage was 95wt% of barite, 3.5 wt% of quartz and 1.5 wt% of hematite (B95Q3.5H1.5) and 87 wt% of barite, 10 wt% of quartz and 3 wt% of hematite (B87Q10H3).
- Iron oxide corrosion products from the high-pressure boiler condensate storage and feed water deaerator.
- Calcium carbonate scale in the form of calcite (CaCO_3).
- The starting materials were manually ground in an agate mortar and a pestle for several minutes to achieve fine particle size^{6,13,15}. Then, the fine deposits were mounted into the XRD sample holder by back pressing.

XRD Data Measurements and Rietveld Calculations

Stepscanned patterns were measured with an X-ray diffractometer (Rigaku Ultima IV) with a copper X-ray tube ($\lambda=1.5406 \text{\AA}$). A monochromator and a proportional detector were used in conjunction with a 0.67° divergence slit, a 0.67° scattering slit, and a 0.3-mm receiving slit at instrument settings of 40 kV and 40 mA. The XRD data were measured from 10° to 140° in 2θ Bragg-angle, using a step size of 0.04° and a counting time of 1° per minute³. Then, the software package (High Score Plus, PANalytical B.V.), combined with the ICDD and powder diffraction file database of the standard reference materials, was used for the phase identification — qualitative analysis — of XRD data of scale and corrosion deposits.

The least-squares structure and profile refinements were performed with the Rietveld refinement program¹⁹. The structural models— crystallographic information file —used for the scale deposits, corrosion deposits, barite, and quartz were taken from the ICSD. The refined parameters were similar to those described by Sitepu et al.¹⁵, and are as follows: phase scale factors, Chebychev polynomial background parameters, lattice parameters, the instrument zero-point, atomic isotropic and anisotropic displacement coefficients, the Lorentzian and the Gaussian terms of a pseudo-Voigt profile function, and the March r -parameter for the crystallographic preferred orientation correction. The results of crystallographic information, such as crystal structure, phase composition, and crystallographic preferred orientation obtained from Rietveld refinement, are given in the next section.

RESULTS AND DISCUSSIONS

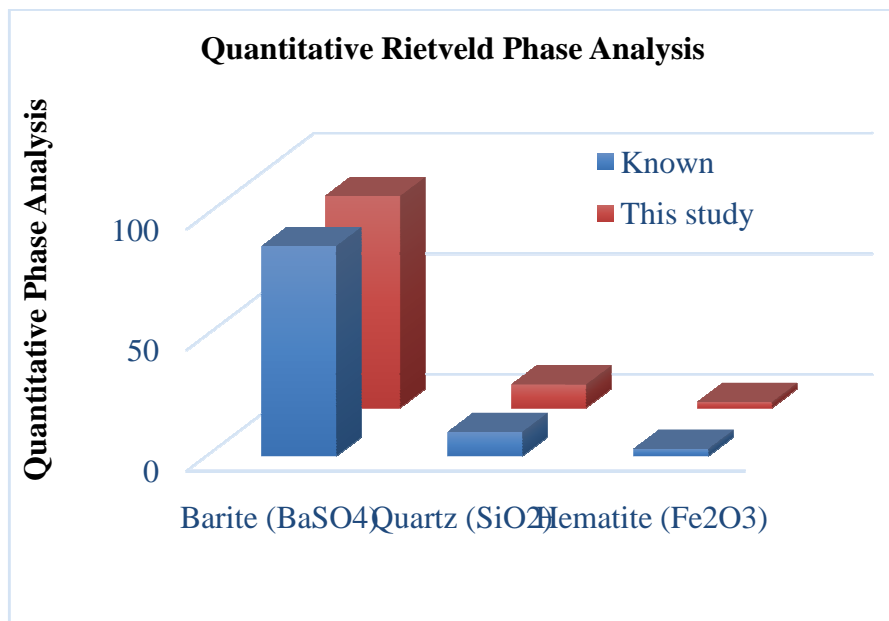
The below results describe the innovative challenge for quantitative Rietveld phase analysis of the (i) known synthetic mix of 95 wt% of barite (BaSO_4), 3.5 wt% of quartz (SiO_2) and 1.5 wt% of hematite (Fe_2O_3), which is denoted B95Q3.5H1.5; (ii) 87 wt% of barite (BaSO_4), 10 wt% of quartz (SiO_2) and 3 wt% of hematite (Fe_2O_3), which is denoted B87Q10H3; (iii) unknown iron oxide corrosion products from the high-pressure boiler condensate storage and feed water deaerator; and (iii) unknown calcium carbonate scale products in the form of calcite (CaCO_3).

Quantitative Rietveld Phase Analysis of Synthetic Mix of the Barite, Quartz, and Hematite Powders (B95Q3.5H1.5 & B87Q10H3)

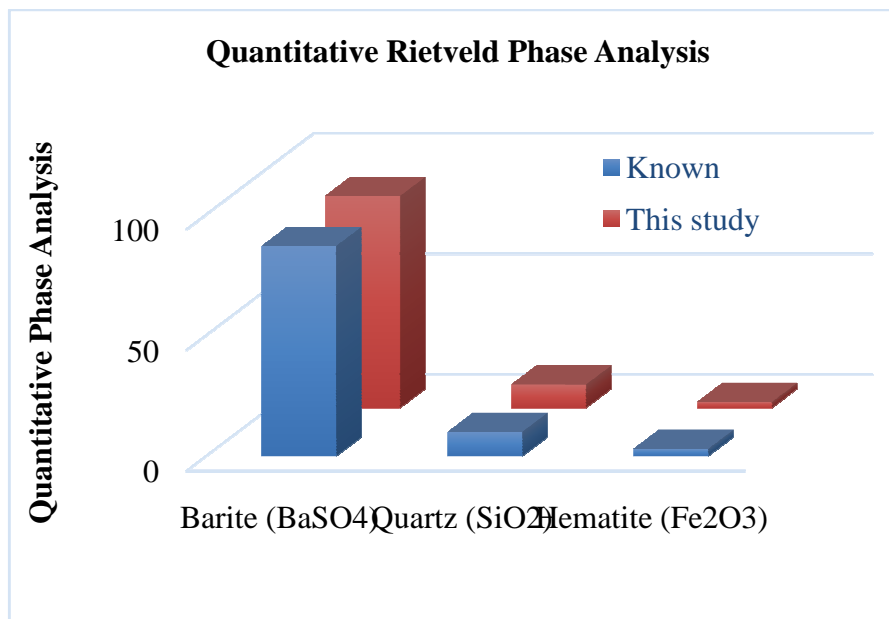
In addition to iron oxide with mineral name of hematite and chemical formula Fe_2O_3 , the silicon oxide with mineral name of quartz and chemical formula SiO_2 that has the International Center Diffraction Data (ICDD, 2018) of the Powder Diffraction File (PDF-4+) database of the standards reference materials appears in almost all of the corrosion products. Therefore, it has been included in the present study. Additionally, the barium sulfate with the mineral name of barite (BaSO_4) is used in the oil drilling industry for lubrication, and therefore, it is of interest primarily in materials characterization research, especially in quantitative Rietveld phase analysis of synthetic mixture. The density and color of this natural mineral make it a valuable product. In each application, the purity and composition of the contaminants should be closely monitored as they may alter the properties and function of the material.

The authors performed Rietveld quantitative analysis of the known mixtures of barite, quartz, and hematite with great care to test the reliability and reproducibility of the Rietveld refinement with the March model for the preferred orientation correction factor. The weight percentage wt% of the known mixture were carefully prepared; 95 wt% of barite (BaSO_4), 3.5 wt% of quartz (SiO_2) and 1.5 wt% of hematite (Fe_2O_3), and denoted B95Q3.5H1.5. The quantitative Rietveld phase analysis results obtained from the Rietveld refinement with the March model for the intensities correction due to the effect of preferred orientation were 94.6(6) wt% for barite, 4.3(8) wt% for quartz and 1.1(2) wt% for hematite, which agreed well with the known values. The number in parentheses gives the estimated standard uncertainty for the least significant figure of the parameter. Subsequently, other known mixtures of 87 wt% of barite, 10 wt% of quartz and 3 wt% of hematite, and denoted B87Q10H3. The corresponding quantitative Rietveld phase analysis results obtained from Rietveld refinement with the March model for preferred orientation correction agreed well with the known values. They were 87.8(7) wt% for barite, 9.6(6) wt% for quartz, and 2.5(5) wt% for hematite, see Figure 1. The summary of the refined structural parameters is given in Tables 1, 2 and 3, which agreed well with the single-crystal XRD data²⁰⁻²⁸. Therefore, it

can be summarized that the quantitative Rietveld phase analysis yields accurate, reliable, and reproducible results for both crystal structure refinement and quantitative analysis of the synthetic mixture of barite, quartz, and hematite.



(a)



(b)

Figure 1: Quantitative Rietveld Phase Analysis Results for (a) 3.5Wt% of Barite, 3.5 wt% of Quartz and 1.5 Wt% of Hematite; and (b) 87 wt% of Barite, 10 Wt% of Quartz and 3 Wt% of Hematite

The authors performed Rietveld quantitative analysis of the known mixtures of barite, quartz, and hematite with great care to test the reliability and reproducibility of the Rietveld refinement with the March model for the preferred orientation correction factor. The weight percentage wt% of the known mixture were carefully prepared; 95 wt% of barite (BaSO₄), 3.5 wt% of quartz (SiO₂) and 1.5 wt% of hematite (Fe₂O₃), and denoted B95Q3.5H1.5. The quantitative Rietveld

phase analysis results obtained from the Rietveld refinement with the March model for the intensities correction due to the effect of preferred orientation were 94.6(6) wt% for barite, 4.3(8) wt% for quartz and 1.1(2) wt% for hematite, which agreed well with the known values. The number in parentheses gives the estimated standard uncertainty for the least significant figure of the parameter. Subsequently, other known mixtures of 87 wt% of barite, 10 wt% of quartz and 3 wt% of hematite, and denoted B87Q10H3. The corresponding quantitative Rietveld phase analysis results obtained from Rietveld refinement with the March model for preferred orientation correction agreed well with the known values. They were 87.8(7) wt% for barite, 9.6(6) wt% for quartz, and 2.5(5) wt% for hematite, see Figure 1. The summary of the refined structural parameters is given in Tables 1, 2 and 3, which agreed well with the single-crystal XRD data²⁰⁻²⁷. Therefore, it can be summarized that the quantitative Rietveld phase analysis yields accurate, reliable, and reproducible results for both crystal structure refinement and quantitative analysis of the synthetic mixture of barite, quartz, and hematite.

Table 1: Summary of the Refined Structure Parameters for Barite (BaSO₄)

Parameters	This Study		Single-Crystal XRD Data
	B95Q3.5H1.5	B87Q10H3	
Ba(x,y,1/4)			
x	0.1580(4)	0.1581(4)	0.15842(2)
y	0.1847(3)	0.1848(3)	0.18453(2)
U	0.0160(6)	0.0149(5)	0.011(4)
S(x,y,3/4)			
x	0.193(1)	0.192(1)	0.19082(9)
y	0.435(1)	0.433(1)	0.43749(7)
U	0.018(3)	0.020(1)	0.009(9)
O1(x,y,3/4)			
x	0.127(3)	0.134(3)	0.1072(4)
y	0.580(3)	0.578(3)	0.5870(3)
U	0.0165	0.0165	0.023(5)
O2(x,y,3/4)			
x	0.034(4)	0.032(4)	0.0498(3)
y	0.311(3)	0.313(3)	0.3176(2)
U	0.0165	0.0165	0.018(6)
O3(x,y,z)			
x	0.312(2)	0.314(2)	0.3118(2)
y	0.409(2)	0.407(2)	0.4194(2)
z	0.909(2)	0.944(3)	0.9704(2)
U	0.0165	0.0165	0.013(2)

Table 2: Summary of the Refined Structure Parameters for Quartz (SiO₂)

Parameters	This Study		Single-Crystal XRD Data
	B95Q3.5H1.5	B87Q10H3	
Si(x,0,1/3)			
x	0.61(1)	0.58(1)	0.53013
U	0.0313	0.056	0.056
O(x,y,z)			
x	0.38(2)	0.385(9)	0.4141
y	0.13(3)	0.14(2)	0.1460
z	0.11(2)	0.11(1)	0.1188
U	0.96	0.096	0.096

Table 3: Summary of the Refined Structure Parameters for Hematite (Fe₂O₃)

Parameters	This Study		Single-Crystal XRD Data
	B95Q3.5H1.5	B87Q10H3	
Fe(0,0,z)			
z	0.1495(5)	0.150(3)	0.1447
U	0.06	0.05	0.05
O(x,0,1/4)			
x	0.3105(3)	0.31(2)	0.3059
U	0.08	0.07	0.07

Quantitative Rietveld Phase Analysis of the Unknown Iron Oxide Corrosion Products from the High-Pressure Boiler Condensate Storage and Feed Water Deaerator

Quantitative Rietveld phase analysis of the known synthetic mix of barite (BaSO₄), quartz (SiO₂) and hematite (Fe₂O₃) was extended to the unknown iron oxide corrosion products from the high-pressure boiler condensate storage and feed water deaerator. The variations in the quantitative Rietveld phase analysis with the identified phases are given in Figure 2 for corrosion products from the high-pressure boiler condensate storage (blue color), and for corrosion products from the high-pressure boiler feed water deaerator (orange color). While iron oxide corrosion product in the form of magnetite [Fe₃O₄] is the major phase for the corrosion deposits in high-pressure boiler condensate storage the other types of iron oxide corrosion products in the form of hematite [Fe₂O₃] is the major phase for the corrosion deposits in boiler feed water deaerator. The total amounts of iron oxide corrosion products in the form of magnetite [Fe₃O₄], hematite [Fe₂O₃] and goethite [FeO(OH)] appeared at the deposits from boiler condensate storage is slightly lower than that of the deposits from boiler feed water deaerator. In other words, the amount of formation material in the form of the quartz phase appeared in the deposits from boiler condensate storage is slightly lower than that of the deposits from boiler feed water deaerator.

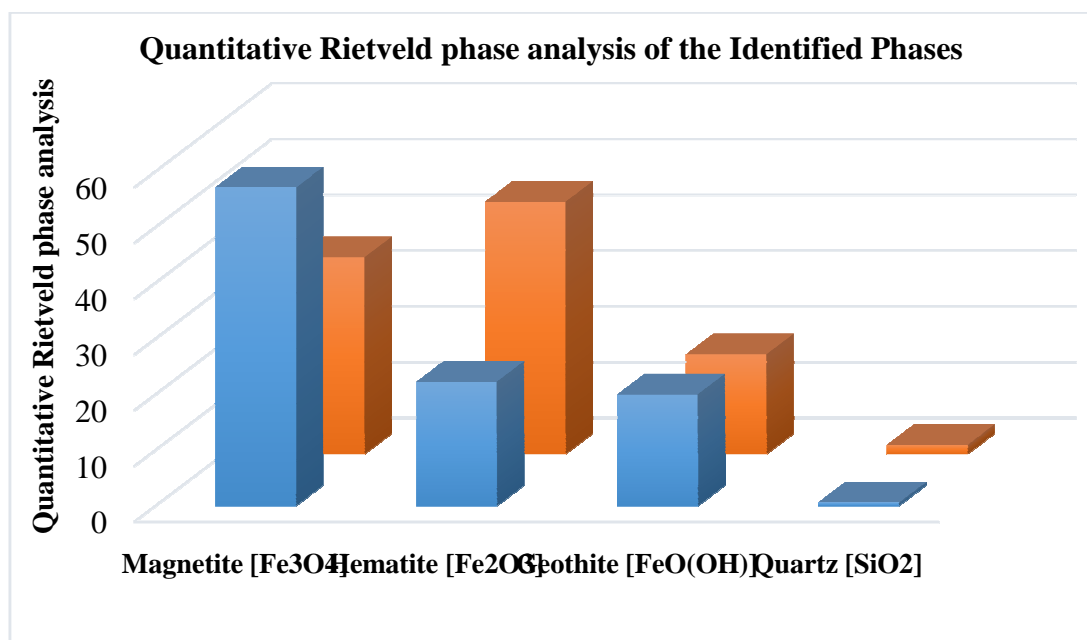
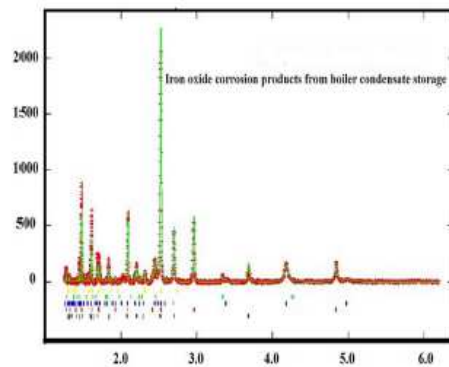


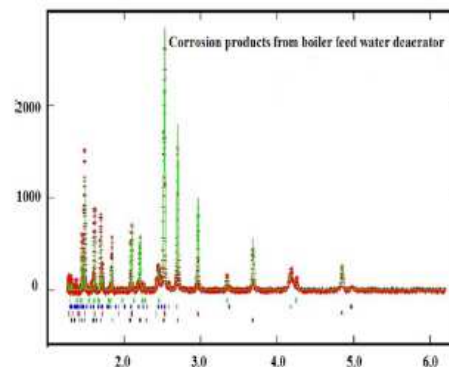
Figure 2: Variation in the Quantitative Rietveld Phase Analyses with the Identified Phases for the Iron Oxide Corrosion Products from the Boiler Condensate Storage (blue color), and Feed water Deaerator (orange color)

Figure 3 shows the agreement between the calculated and measured XRD patterns for the iron oxide corrosion products from the boiler (a) condensate storage, and (b) feed water deaerator, following Rietveld refinement with the March model for crystallographic preferred orientation correction. The observed data are indicated by a plus sign and the calculated profile is the solid line in the same field. The sets of vertical lines below the profiles represent the positions of all possible Bragg reflections for each phase.

The crystallographic preferred orientation correction factors of the corrosion deposits in the form of magnetite [Fe_3O_4] and hematite [Fe_2O_3] for the deposits from boiler condensate storage are lower than the corresponding values for the corrosion deposits in the form of magnetite [Fe_3O_4] and hematite [Fe_2O_3] for the deposits from boiler feed water deaerator. Therefore, it can be summarized that the corrosion deposits from boiler feed water deaerator has crystallographic preferred orientation (or texture of crystalline materials), and therefore, the XRD intensities of the corrosion deposits have to be corrected due to the preferred orientation by using the Rietveld refinement with the March model both for the quantitative phase analysis (phase composition) and the crystal structure refinement.



(a) Corrosion Products from Boiler Condensate Storage



(b) Corrosion Products from the Boiler Feed Water Deaerator

Figure 3: The Agreement between the Calculated and Measured XRD Patterns for the Deposits from the Boiler (a) Condensate Storage, and (b) Feed Water Deaerator, Following Rietveld Refinement with the March Model. The Observed Data are Indicated by a Plus Sign and the Calculated Profile is the Solid line in the Same Field. The Sets of Vertical Lines below the Profiles Represent the Positions of All Possible Bragg Reflections for Each Phase

Structural and Texture Characterization of Calcium Carbonate Scale Deposits from Boiler Tubes in Refinery

The Quantitative Rietveld phase analyses of the known synthetic mix of barite (BaSO_4), quartz (SiO_2) and hematite (Fe_2O_3), and unknown natural iron oxide corrosion products from the high-pressure boiler condensate storage and feed water deaerator was extended to the structural and texture characterization of calcium carbonate scale deposits from boiler tubes in refinery, see Figure 4. The refined structural parameters obtained from the Rietveld refinement agreed well with the single-crystal XRD data results and powder XRD results for calcite [CaCO_3]²⁰. The space group used was R-3c (No. 167). Wyckoff coordinates: 6(c) are 0,0,0 and 0,0,1/2; 6(a) are 0,0,3/4; and 18(e) are x,0,1/4; -x,-x,1/4;-x,0,3/4;0,-x,3/4, and x,x,3/4. The cell formula unit is Z=6, and the formula weight =100.09. Details of the referenced cell parameters are given^{15,20}.

The agreement between the calculated and measured XRD pattern for the calcium carbonate scale in the form of calcite (CaCO_3) following Rietveld refinement with the March model is given in Figure 4. Figure 5 shows the plots of the March preferred orientation corrections with an orientation angle derived from the Rietveld refinement with the March model when the $\langle 104 \rangle$ was used as the preferred orientation direction. In the case of an ideal random orientation, the March preferred orientation correction factor is unity, Table4 and Figure 5. As expected for the XRD data for the carbonate scale deposits with the refined March preferred orientation parameter, $r=0.854(7)$, which is less than 1.00 (Table 4), the March preferred orientation correction factor is maximum at the orientation angle $\phi = 0^\circ$ and minimum at $\phi = 90^\circ$. The crystallographic figures-of-merit (R_p , R_{wp} , $R(F^2)$) and goodness-of-fit index (χ^2) obtained from Rietveld refinement with the March model are $R_p = 9.75$, $R_{wp} = 13.30$, $R(F^2) = 10.15$, and $\chi^2 = 1.32$; and the March preferred orientation parameter is 0.854(7).

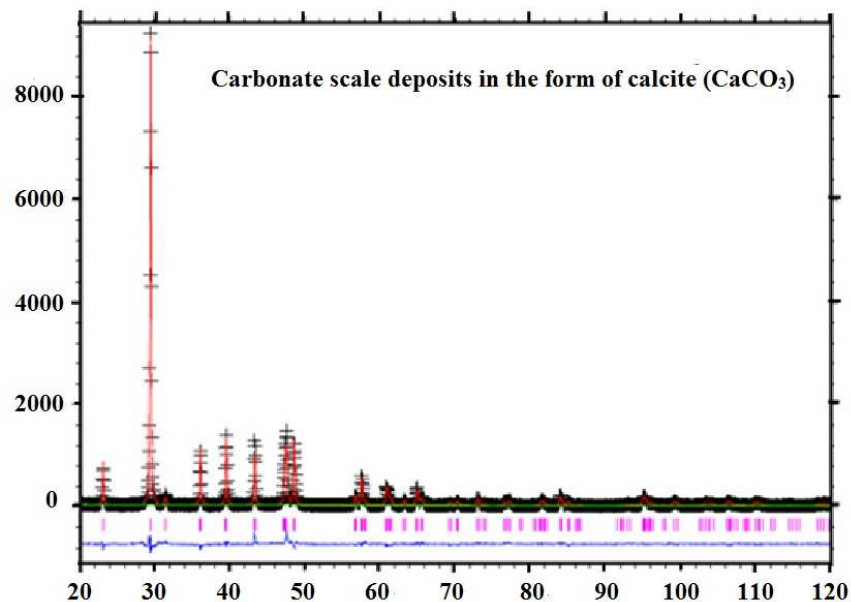


Figure 4: The agreement between the calculated and measured XRD patterns for the carbonate scale deposits in the form of calcite (CaCO_3) following Rietveld refinement with the March model for preferred crystallographic orientation correction.

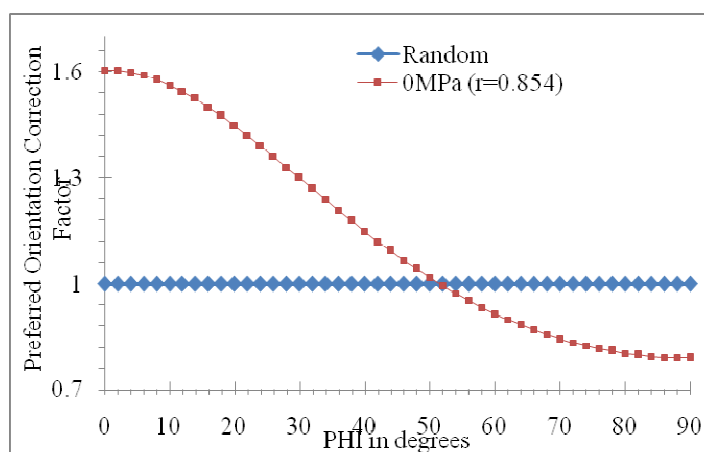


Figure 5: The variation of the March preferred crystallographic orientation corrections with an orientation angle. The $\langle 104 \rangle$ was used as the preferred orientation direction in the Rietveld refinement. The March preferred orientation parameter is 0.854, whereas the March r-parameter for random orientation materials is 1.000.

Table 4: Summary of the Refined Atomic Positions of Calcite (CaCO_3)

Atomic Positions	This Study	Single Crystal XRD Data ²⁰
a (Å)	4.97630(15)	4.988(2)
c (Å)	17.0904(9)	17.068(2)
V (Å) ³	366.520(31)	367.8(3)
Ca(0,0,0)U _{iso}	0.0162(5)	0.00988(3)
C(0,0,1/4)U _{iso}	0.0110(16)	0.00834(9)
O(x,0,1/4)xU _{iso}	0.2544(4) 0.0247(9)	0.25700(6) 0.01129(7)
R _p	9.75	
R _{wp}	13.30	
R(F ²)	10.15	
χ ²	1.32	
r	0.854(7)	

Table 4 depicts the unit cell parameters of the carbonate scale in the form of calcium carbonate scale in the form of calcite (CaCO_3) obtained from the Rietveld refinement with the March model. The number in parentheses gives the estimated standard uncertainty for the least significant figure of the parameter. The refined structural parameters (Table 4), including the unit cell agreed well with the corresponding single-crystal XRD and powder XRD results for calcite (CaCO_3)²⁰, which indicate that the Rietveld refinement yields the reproducibility of the structural and quantitative analysis results.

In the present study, the authors described the quantitative Rietveld phase analysis of the known synthetic mixtures of drilling mud in the form of barium sulfate with the mineral name barite (BaSO_4), formation material in the form of silicon oxide mineral name quartz (SiO_2) and iron oxide mineral name hematite (Fe_2O_3); the unknown natural corrosion products from the high-pressure boiler condensate storage and feed water deaerator; and the structural and texture characterization of calcium carbonate scale in the form of calcite (CaCO_3). Based on the results, it can be summarized that: Quantitative Rietveld phase analysis results for the synthetic mixed of barite, quartz, and hematite that were prepared independently agreed well with the known wt% of the mixture samples, which indicate that the Rietveld refinement yields the accurate and quick of the structural and quantitative phase analysis results²⁰⁻²⁹. Obtaining accurately

and quickly the quantitative analysis results for the crystalline materials part of corrosion and scale products are certainly important for the field engineers at the refineries and gas plants to facilitate chemical cleaning and prevent the reoccurrence to stop the generation of those particular deposits.

Please note the preliminary results of this paper was previously presented at the 15th Middle East Corrosion Conference & Exhibition, held in the Kingdom of Bahrain, on February 2-5, 2014.

CONCLUSIONS

It can therefore be concluded that the quantitative Rietveld phase analysis of synthetic mixture powders, iron oxide corrosion products, and calcium carbonate scale deposits from the refinery and gas plants yields

- Accurate, quick, reliable, and reproducible results,
- Good agreement between the measured and calculated of the all XRD data sets, and
- The refined structural parameters of all data sets agreed well with the XRD single crystal results

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REFERENCES

1. Smith, S.N.: "Corrosion Product Analysis in Oil and Gas Pipelines," *Chemical Treatment*, July 7, 2004.
2. Sitepu, H. and Zaidi, S.R.: "Application of a New Method in Identifying the Sludge Deposits from Refineries and Gas Plants: A Case of Laboratory-Based Study," *International Journal of Corrosion*, Vol. 2017, Article ID 9047545, 7 pages, <https://doi.org/10.1155/2017/9047545>.
3. Sitepu, H. and Zaidi, S.R.: "Application of X-ray Powder Diffraction and Rietveld Phase Analysis to Support Investigations of Failure for Submersible Pump," *Saudi Aramco Journal of Technology*, Winter Edition, 2017.
4. Bish, D.L. and Howard, S.A.: "Quantitative Phase Analysis Using the Rietveld Method," *Journal of Applied Crystallography*, Vol.21, 1988, pp. 86-91.
5. Hill, R.J. and Howard, C.J.: "Quantitative Phase Analysis from Neutron Powder Diffraction Data Using the Rietveld Method" *Journal of Applied Crystallography*, Vol. 20, 1987, pp. 467-474.
6. O'Connor, B.H. and Raven, M.D.: "Application of the Rietveld Refinement Procedure in Assaying Powdered Mixtures," *Powder Diffraction Journal*, Vol. 3, No. 4, 1988, pp. 2-6.
7. Scarlett, N.V.Y., Madsen, I.C., Cranswick, L.M.D., et al.: "Outcomes of the International Union of Crystallography Commission on Powder Diffraction Round Robin on Quantitative Phase Analysis: Samples 2, 3, 4, Synthetic Bauxite, Natural Granodiorite and Pharmaceuticals," *Journal of Applied Crystallography*, Vol.35, No. 4, 2002, pp. 383-400.
8. Rietveld, H.M.: "A Profile Refinement Method for Nuclear and Magnetic Structures," *Journal of Applied Crystallography*, Vol. 2, 1969, pp. 65-71.

9. Mccusker, L.B., Von Dreele, R.B., Cox, D.E., Louer, D. and Scardi, P.: "Rietveld Refinement Guidelines," *Journal of Applied Crystallography*, Vol. 32, No. 1, 1999, pp. 36-50.
10. Hewat, A., David, W.I. and van Eijck, L.: "Hugo Rietveld(1932–2016)," *Journal of Applied Crystallography*, Vol. 49, No. 4, 2016, pp. 1394-1395.
11. Bunge, H.J.: "Texture Analysis in Materials Science: Mathematical Methods" Butterworths-Heinemann, London, 1982.
12. Dollase, W.A.: "Correction of Intensities for Preferred Orientation in Powder Diffractometry: Application of the March Model," *Journal of Applied Crystallography*, Vol. 19, 1986, pp. 267-272.
13. O'Connor, B.H., Li, D.Y. and Sitepu, H.: "Strategies for Preferred Orientation Corrections in X-ray Powder Diffraction Using Line Intensity Ratios," *Advances in X-ray Analysis*, Vol. 34, 1991, pp. 409-415.
14. Popa, N.C.: "Texture in Rietveld Refinement," *Journal of Applied Crystallography*, Vol. 25, 1992, pp. 611-616.
15. O'Connor, B.H., Li, D.Y. and Sitepu, H.: "Texture Characterization in X-ray Powder Diffraction Using the March Formula," *Advances in X-ray Analysis*, Vol. 35, 1992, pp. 277-283.
16. Järvinen, M.: "Application of Symmetrized Harmonics Expansion to Correction of the Preferred Orientation Effect," *Journal of Applied Crystallography*, Vol. 26, 1993, pp. 525-531.
17. Von Dreele, R.B.: "Quantitative Texture Analysis by Rietveld Refinement," *Journal of Applied Crystallography*, Vol. 30, 1997, pp. 517-525.
18. Sitepu, H.: "Texture and Structural Refinement Using Neutron Diffraction Data from Molybdenite (MoO_3) and Calcite (CaCO_3) Powders and a Ni-rich $\text{Ni}_{50.7}\text{Ti}_{49.30}$ Alloy," *Powder Diffraction*, Vol. 24, 2009, pp. 315-326.
19. Larson, A.C. and von Dreele, R.B.: "General Structure Analysis System (GSAS)," Report LAUR 86-748, Los Alamos, New Mexico: Los Alamos National Laboratory, 2000.
20. Maslen, E.N., Streltsov, V.A., Streltsova, N.R. and Ishizawa, N.: "Electron Density and Optical Anisotropy in Rhombohedral Carbonates. III. Synchrotron X-ray Studies of CaCO_3 , MgCO_3 and MnCO_3 ," *Acta Crystallography*, Vol. B51, 1995, 929-939.
21. Antao, S.M., Hassan, I., Wang, J., Lee, L.P. and Toby, B.H.: "State-of-the-Art High-Resolution Powder X-ray Diffraction (HRPXRD) Illustrated with Rietveld Structure Refinement of Quartz, Sodalite, Tremolite and Meionite," *Canadian Mineralogist*, Vol. 46, 2008, pp. 1501-1509.
22. Al-Ghamdi, R.A. and Sitepu, H.: "Structural and Quantitative Phase Analysis of XRD Data of Sludge Deposits from Refineries and Gas Plants by Using the Rietveld Method," *Saudi Aramco Journal of Technology*, 2018 Winter Edition, 2018, 18, 41-48.
23. Al-Ghamdi, R.A. and Sitepu, H.: "Characterization of Sludge Deposits from Refineries and Gas Plants: A Prerequisite Results Requirements to Facilitate Chemical Cleaning of the Particular Equipment," *International Journal of Corrosion* 2018. (Article ID 4121506), 2018, 9 page. <https://doi.org/10.1155/2018/4121506>.

24. Sitepu, H. and Al-Ghamdi, R.A.: "Quantitative Phase Analysis of XRD Data of Sludge Deposits from Refineries and Gas Plants by Use of the Rietveld Method," *Advances in X-Ray Analysis*. Vol 62. 2019, In print.
25. Sitepu, H., Al-Ghamdi, R.A., and Zaidi, S.: "Corrigendum to "Application of a New Method in Identifying the Sludge Deposits from Refineries and Gas Plants: A Case of Laboratory-Based Study," *International Journal of Corrosion* 2018. (Article ID 8646104), 2018, 1 page <https://doi.org/10.1155/2018/8646104>.
26. Sitepu, H. and Al-Ghamdi, R.A.: "Application of the Rietveld Method to the Analysis of XRD Data of Scale and Corrosion Deposits Formed in Oil and Gas Pipelines," *IMPACT: International Journal of Research in Engineering & Technology*, ISSN (P):2347-4599; ISSN (E):2321-8843; Impact Factor (JCC): 3.9074,6(8), 2018, pp. 67-78.
27. Sitepu, H., Al-Ghamdi, R.A., Zaidi, S and Shen, S.: "Use of the Rietveld method for describing structure and texture in XRD data of scale deposits formed in oil and gas pipelines: an important industrial challenge," *Advances in X-Ray Analysis*, 58, 2015. Pp. 41-50.
28. Sitepu, H. and Al-Ghamdi, R.A.: "Use of the Rietveld method for describing structure and texture in XRD data of dolomite [$\text{CaMg}(\text{CO}_3)_2$] and hydromagnesite [$[\text{Mg}_5(\text{CO}_3)_4(\text{OH})_2(\text{H}_2\text{O})_4]$]," *Advances in X-Ray Analysis*, 56, 2013, pp.137-145.
29. Sitepu, H., O'Connor, B.H. and Li, D.Y.: "Comparative Evaluation of the March and Generalized Spherical Harmonic Preferred Orientation Models Using X-ray Diffraction Data for Molybdenite and Calcite Powders," *Journal of Applied Crystallography*, 38, 2005, pp. 158-167.