Lab Report XRD 76

X-Ray Diffraction Analysis in the Petroleum Industry: Scales and Corrosion Products

Summary

X-ray diffraction (XRD) is a powerful analytical tool that can be used to identify crystalline materials and quantify weight fractions in samples with multiple phases. In the petroleum industry, XRD finds use in a wide range of applications including: mineralogy and whole rock analysis, speciation and quantification of clay fractions, catalyst characterization, fly ash beneficiation, and analysis of scales and corrosion products.

In this report, we will focus on the latter of these applications and demonstrate the use of desktop XRD technology for qualitative and quantitative analysis of mineralogical scales and corrosion materials.

Introduction

Scaling is the deposition of solid material from a solution or suspension. The conditions that determine scaling formation and buildup are complex and dependent on a number of variables, including the type and concentration of dissolved gases and ions, temperature, pressure, pH, and salinity. From a production standpoint, scaling and fouling present a significant challenge to the petroleum industry, as deposits can swiftly lead to reduced flow rates within tubing and valves as well as complete blockage of the wellbore. Examples of this can be seen in Figure 1, which illustrates the varying thickness – and concurrent reduction in pipe volume – of two sample scale deposits.

Figure 1: Two scale deposits that were mechanically removed from pipe segments for analysis and testing.

Table 1 provides a representative list of several commonly observed industrial scales and corrosion products. This list contains many of the frequently identified materials, such as calcium carbonate and barium sulfate, but is not intended to serve as an exhaustive listing. The phases present in any given scale will depend on the formation conditions as well as the specific drilling or production site. For example, halite scales can form during rapid quenching of seawater while carbonate production can occur via precipitation reactions when mixing of incompatible water sources. Additional sources of solid matter include the presence of phyllosilicate clays and residual drilling muds.

Table 1: A list of several common industrial scales and corrosion products.

Mineralogical Name	Chemical Formula	Classification
Calcite	$CaCO_3$	Carbonate
Aragonite	$CaCO_3$	Carbonate
Anhydrite	$CaSO_4$	Sulfate
Bassanite	$2CaSO_4 \cdot H_2O$	Sulfate
Gypsum	$CaSO_4 \cdot 2H_2O$	Sulfate
Halite	NaCl	Salt
Brucite	$Mg(OH)_2$	Hydroxide
Baryte (Barite)	$BaSO_4$	Sulfate
Celestine	$SrSO_4$	Sulfate
Amorphous Silica	SiO_2	Oxide
Quartz	SiO_2	Oxide
Wustite	FeO	Oxide
Hematite	Fe_2O_3	Oxide
Maghemite	Fe_2O_3	Oxide
Magnetite	Fe_3O_4	Oxide
Goethite	FeO(OH)	Oxyhydroxide
Lepidocrocite	FeO(OH)	Oxyhydroxide
Akaganeite	FeO(OH)	Oxyhydroxide
Siderite	$FeCO_3$	Carbonate
Cuprite	Cu_2O	Oxide
Tenorite	CuO	Oxide

Figure 2: The D2 PHASER desktop diffractometer

reduced structural integrity due to increased brittleness.

With both classes of materials (scales and corrosion products), the ultimate goals in characterization are to develop appropriate courses of treatment, removal, and prevention and to minimize costly repairs and downtime. In this report, we will address both mineralogical scales as well as chemical corrosion products, both of which can be positively identified and quantified using X-ray diffraction.

Experimantal

Specimens were prepared by crushing the collected samples to coarse granules and then grinding to a fine powder (< 325 mesh) with an agate mortar and pestle. Larger volume or gram-scale samples can be processed using mechanical attrition equipment, such as crushing apparati or shaker mills.

Materials were analyzed using a D2 PHASER diffractometer (Figure 2) with a LYNXEYE detector. Both copper (Cu) and cobalt (Co) tubes were used in this study, although the primary source of radiation was copper. Diffraction data were analyzed using two separate software packages: DIFFRAC.EVA for phase identification and DIFFRAC.TOPAS for phase quantification via Rietveld refinement.

Various sample holders were employed throughout this study to accommodate a wide range of sample types. Most samples were prepared using a back-loading technique to reduce the effects of preferred orientation. For smaller volume samples, powdered material was dusted onto a low-background silicon wafer prior to analysis.

Data collection times ranged from 5 minutes to 1 hour, depending on the amount of available material as well as the individual sample scattering potential, which includes contributing factors such as sample crystallinity and atomic composition.

The term "scale" is often used to refer to both mineralogical scales, which typically form via precipitation, and chemical corrosion products, which typically form via oxidative reactions. Corrosion products – often metal chalcogenides or carbonates – are distinct from mineralogical scales in that a metallic component of the production facility (e.g. piping, valves, or propellers) generally serves as one of the constituent chemical reactants. This can occur via leaching and subsequent precipitation or through direct formation of corrosion phases. In addition to the potential for blockages, corrosion also presents the additional problem of failure or

Analysis of Mineralogical Scales

Given the large number of scaling materials, identification of various species is of the utmost importance, particularly for determining both the cause of scaling as well as the appropriate courses of treatment and prevention. Depending on the composition of the deposited scale, removal options may include (1) treatment with acidic fluids, (2) binding of ions via chelation, or (3) physical removal with water jetting or abrasive formulations. For example, calcium carbonate is highly susceptible to removal by acid washing, while barium sulfate demonstrates resistance to most chemical approaches.

One relevant example of this concept is the polymorphism of calcium carbonate. Two of the polymorphs of $CaCO_3$, calcite and aragonite, can form under different local environments. Aragonite, while possessing a higher density and hardness than calcite, is generally preferred due to the formation of softer scales that are more easily removed and the tendency of precipitates to stay suspended in the liquid phase. Diffraction data for several calcium-containing scales is shown in Figure 3. Of the three analyzed scales, one is primarily composed of calcite, another primarily composed of aragonite, and a third contains both polymorphs as well as some halite. Knowledge of specific phase compositions can provide insight into formation mechanisms and can also be applied to develop tailored approaches for treatment.

For complex mixtures, quantification of individual phases can be achieved following the identification of each mineralogical component. Figure 4 describes the various calcium sulfate phases identified in a collected powdered scale. The relative weight percentages of each identified phase were calculated using a quantitative Rietveld approach (Figure 5). DIFFRAC.TOPAS allows for the development of robust refinement models that account for a number of variables, including instrumental contributions and preferred orientation, which is strongly exhibited by gypsum.

Figure 4: Qualitative analysis of a calcium sulfate scale. Identified phases include various hydrates (bassanite and gypsum) as well as some calcium carbonate (aragonite and calcite).
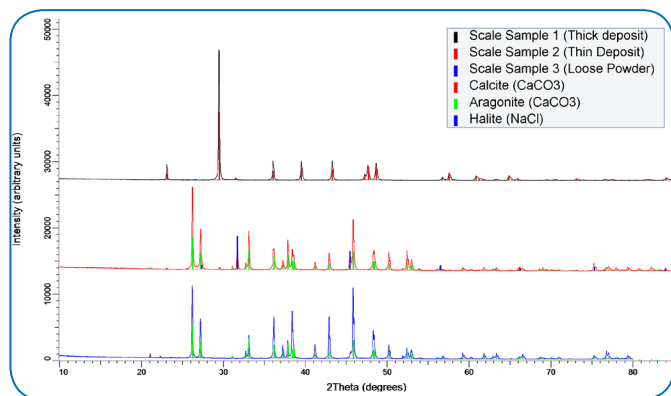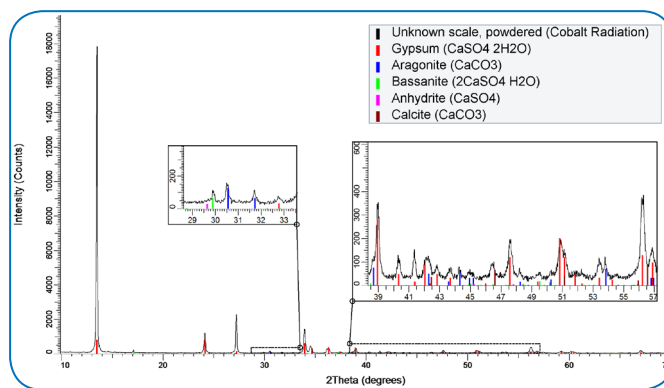

Figure 3: Qualitative analysis of three different calcium carbonate scales. The top scan indicates a scale that is primarily calcite. The bottom scan is from a scale that is primarily aragonite. The middle data set is composed of both polymorphs (calcite and aragonite) as well as some halite.
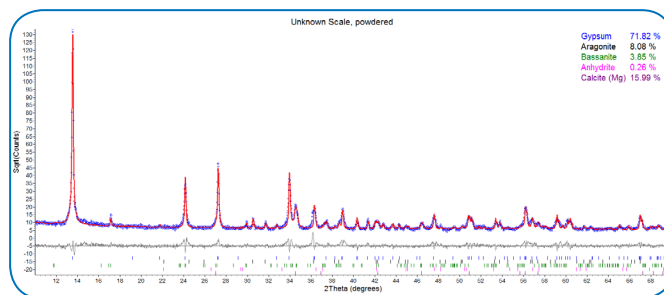

Figure 5: Quantitative analysis of crystalline phases within a mixed phase calcium sulfate scale. The diffraction scan is plotted in a square root scale (y-axis) to demonstrate the fit between calculated and raw data.

Analysis of Corrosion Products

As mentioned previously, corrosion products can be considered distinct from deposited mineralogical scales, though they may result in similar blockages in drill-site and production components. Many factors can contribute to these reactions, including pH and the concentration of dissolved oxygen, carbon dioxide, and hydrogen sulfide.

In this experiment, we analyzed metallic corrosion phases recovered from a failed water boiler. Diffraction data (Figure 6) show the presence of several iron corrosion products with varying oxidation states, including hematite and goethite.
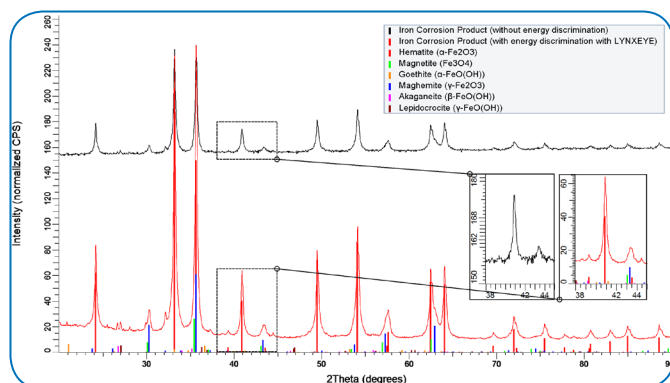

Figure 6: X-ray diffraction data for a sample of corroded iron without energy discrimination (top scan, black) and with energy discrimination (bottom scan, red). Optimizing detector settings on the LYNXEYE reduces iron fluorescence and provides a gain in peak-to-background ratios, in this case a 10-fold improvement. Database patterns for the identified oxide and oxyhydroxide phases are provided for reference along the x-axis.

Iron-containing materials can be challenging to analyze using diffractometers equipped with scintillation counters due to sample fluorescence and resulting high background. Advanced detectors, such as the LYNXEYE 1-D detector, allow for the reduction in fluorescent background and lead to greatly improved peak-to-background ratios while maintaining the advantages of higher data collection speeds. For this sample, the LYNXEYE results in a 10-fold increase in peak-to-background ratio.

Conclusion

XRD can be used in the qualitative and quantitative analysis of industrial scales and corrosion products, providing an insight into the composition of deposited phases. X-ray diffraction often serves as a complementary analytical technique to elemental analysis (e.g. X-ray fluorescence) to provide a more exhaustive characterization and to discrimination between materials with similar chemical compositions, such as (1) pyrite and hematite or (2) calcite and aragonite. This information can then be used to develop a tailored approach for the systematic treatment, removal, and prevention of industrial scales.

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