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Corrosion Deposits Data Base - X-Ray Diffraction Analysis of Deposits from Oil and Gas Upstream Well/Production systems

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ABSTRACT

This paper presents the analysis results of a wide range of corrosion deposits, scale deposits, and sludge collected from various components within the oil and gas upstream well/production systems. The accumulation of corrosion deposits within equipment can lead to catastrophic failures and unplanned shutdowns of well/production operations. Therefore, understanding the nature of these deposits and identifying their composition is crucial. This study aims to identify the phases and compounds present in corrosion deposits and determine their source. Furthermore, the identification and characterization of these deposits assist clients in determining the underlying causes of corrosion, enabling the development of effective corrosion mitigation strategies. The X-ray Powder Diffraction (XRD) data presented in this paper serves as a valuable resource for clients during major problems and shutdowns, as no comprehensive database of this nature currently exists. The paper also outlines the sample preparation and analysis procedures employed to examine these corrosion deposits thoroughly.

Keywords: XRD analysis, sludge, corrosion deposits, scale deposits, plant shutdown, corrosion, and phase identification.

INTRODUCTION

Operators in the oil and gas industry worldwide are facing significant challenges in managing corrosion and deposits, such as scale, wax, and paraffin, which negatively impact well production and require additional maintenance and intervention. These challenges are the common issue among most of the operators worldwide. These problems can lead to decreased efficiency and productivity, and can also cause damage to equipment, leading to costly repairs or replacements. Thus, it is important for operators to take proactive measures to address and prevent corrosion and deposit buildup in order to ensure the longevity and optimal performance of their wells.

It is noteworthy that operators frequently rely on chemical treatments to address corrosion and deposit control challenges, however, these treatments may not be highly effective. Additionally, inadequate effectiveness of chemical treatments is a significant contributor to artificial lift failures and could further exacerbate the negative impact on well performance The paper provides case studies on some corrosion products collected from the well and the information of the corrosion products presented in the case studies could aid service providers in enhancing the effectiveness of chemical treatments and their delivery methods. The chemical treatment program was in place for the wells where corrosion products were collected. The samples were collected from the wells that were operational for a certain period before being temporarily shut down for an intervention job.

The corrosion deposits discussed in this case are collected from drive down bailers. A drive down bailer is a specialized tool that is used in the drilling process for oil and natural gas. It is utilized to remove cuttings, which are small pieces of rock and debris that are generated during the drilling process, from the bottom of the borehole. The tool is lowered into the borehole on a drill string and is then activated to create a suction that draws cuttings up and out of the borehole. This suction is created by the tool's internal components and is typically powered by a hydraulic system.

Drive down bailers are typically used in conjunction with other drilling tools, such as drilling fluids and drilling bits. These tools work together to create a stable and clean drilling environment. They also help to extend the life of the drilling equipment and to reduce the overall cost of drilling.

XRD analysis technique was used to identify the phases/composition of the collected corrosion products. XRD is a nondestructive (NDT) technique that provides detailed information about the crystallographic structure, chemical composition, and physical properties of a material.[1-2] Prior to testing, the samples were ground with a mortar and pestle, and then back loaded into standard sample holders. Diffraction scans were then run on a Powder diffractometer using Cu radiation at 45KV/40mA over the range of 6° - 80° with a step size of 0.0167° and an accumulated counting time of 250 seconds per step. Once the diffraction patterns had been obtained, the phases were identified with the aid of the Powder Diffraction File published by the International Centre for Diffraction Data or the Inorganic Crystal Structure Database. For better understanding, the obtained diffraction patterns are shown full scale and at exploded views to better show the minor peaks. The quantitative analyses of the identified phases were performed with a Rietveld refinement.

CASE HISTORY 1: CORROSION DEPOSITS COLLECTED AT DIFFERENT DEPTHS

XRD ANALYSIS OF DEPOSITS COLLECTED FROM THE SAME WELL BUT AT DIFFERENT DEPTHS

Both the corrosion deposits were black in color and the deposit collected at 14219 feet is finer compared to the deposit collected at 14204 feet. There is no obvious odor of rotten egg from the deposits. The XRD data is shown in the Table 1 below, and the XRD spectrums are shown in Figures 1 and 2.

Table 1
Crystalline Phase Analysis (wt. %)

	Deposit collected at Depth: 14204 Ft (sample 2)	**Deposit collected at Depth: 14219 Ft (sample 1)**
$BaSO_4$ (Barite)	26.9	38.9
W (Tungsten)	6.8	0.3
$CaSO_4$ (Anhydrite)	13.7	9.6

PbS (Galena)	3.3	0.6
WS_2 (Tungstenite)	0.7	--
$CaMg(CO_3)_2$ (Dolomite)	16.3	32.5
$CaCO_3$ (Calcite)	3.5	14.4
NaCl (Halite)	3.0	1.2
SiO_2 (Quartz)	7.7	2.5
$CaCO_3$ (Aragonite)	12.6	--
$Cu_6As_4S_9$ (Sinnerite)	5.5	--
$Mg_4Al_2(OH)_{12}CO_3\cdot 3H_2O$ (Quintinite)	--	--

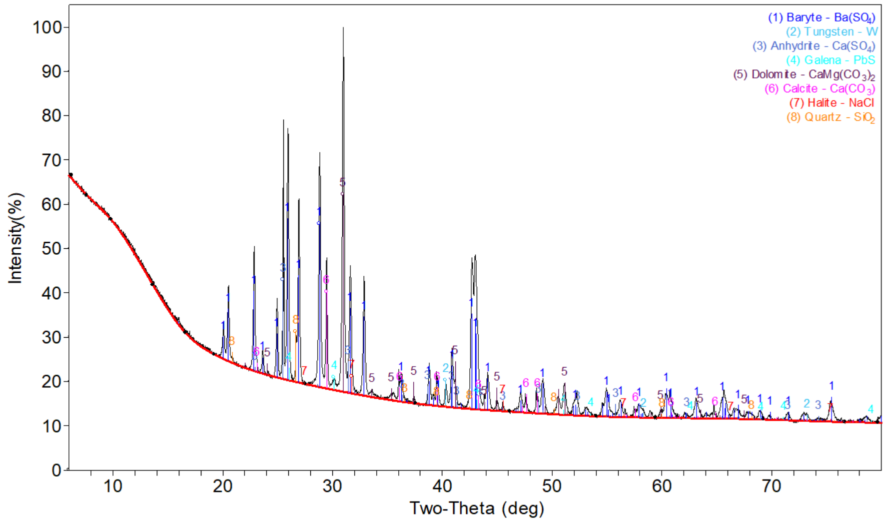

Figure 1a: Phase identification for sample 01.

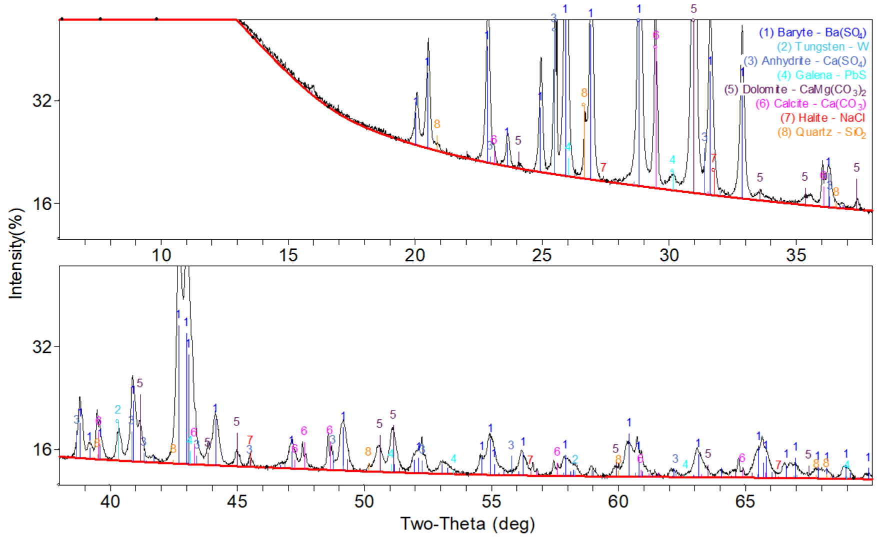

Figure 1b: Exploded view of phase identification for sample 01.

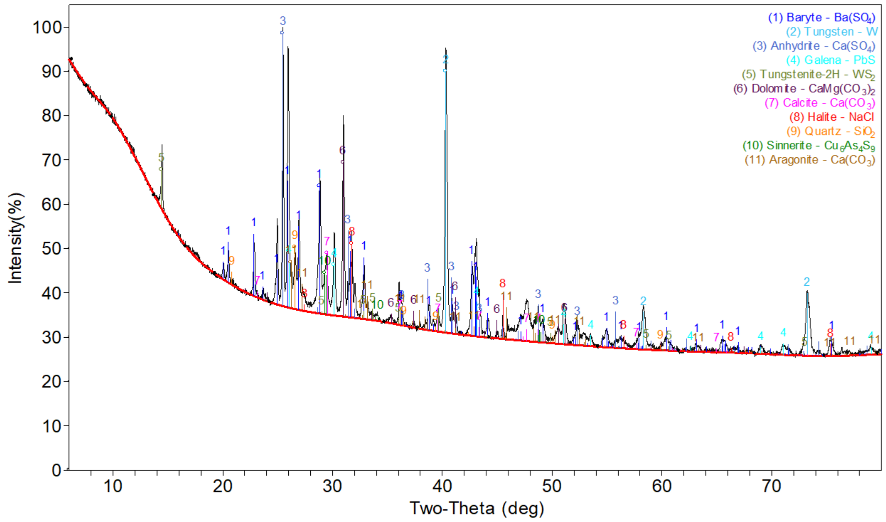

Figure 2a: Phase identification for sample 02.

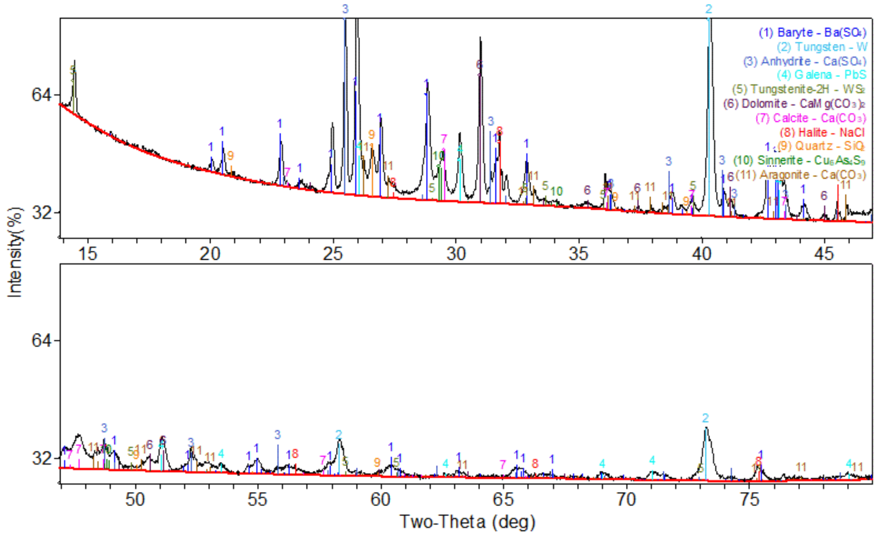

Figure 2b: Exploded view of phase identification for sample 02.

SUMMARY OF FINDINGS OF CASE STUDY 1

The source of these corrosion deposits found in an oil and gas well could be a combination of various factors, including the geology of the formation, the composition of the fluids present in the well, and the conditions under which the well is operating.

1. $BaSO_4$ (Barite) is often used as a weighting agent in drilling fluids, which may contribute to its presence in the well.
2. W (Tungsten) and WS_2 (Tungstenite) could be corrosion by-products of tungsten carbide cutting tools or other equipment that was used during drilling or completion of the well.
3. $CaSO_4$ (Anhydrite) and NaCl (Halite) could be present as a result of the interaction of formation fluids and drilling fluids with evaporite formations in the subsurface.
4. PbS (Galena) and $Cu_6As_4S_9$ (Sinnerite) could be present as a result of corrosion of lead or copper-based alloys that are commonly used in well construction.

5. $CaMg(CO_3)_2$ (Dolomite), $CaCO_3$ (Calcite), SiO_2 (Quartz), $CaCO_3$ (Aragonite) and $Mg_4Al_2(OH)_{12}CO_3 \cdot 3H_2O$ (Quintinite) could be present as a result of interaction of fluids with the subsurface formation.
6. The absence of iron in the deposits, combined with the presence of minerals typical of evaporite and carbonate formations, suggests that the well might be located in a sedimentary basin characterized by these geological features. The use of corrosion-resistant materials and effective corrosion management practices are likely contributing to the absence of iron-based corrosion products.

CASE HISTORY 2: CORROSION DEPOSITS COLLECTED AT A DEPTH OF 10814 FEET

XRD ANALYSIS OF DEPOSITS COLLECTED FROM A DIFFERENT WELL

The corrosion deposit was collected from a different well. The deposit was black in color and in cluster forms. There is a strong odor of rotten egg from the deposits. The XRD data is shown in Table 2 below, and the XRD spectrums are shown in Figure 3.

Table 2
Crystalline Phase Analysis (wt. %)

	Deposit collected at Depth: 10814 Ft (sample 3)
$FeCO_3$ (Siderite)	41.9
Fe_7S_8 (Pyrrhotite) or similar stoichiometry	20.2
$Fe_2(CO_3)(OH)_2$ (Chukanovite)	19.1
FeS (Mackinawite)	10.1
FeO(OH) (Goethite)	4.5
FeS (Trollite)	2.1
FeO(OH,Cl) (Akaganeite)	2.1

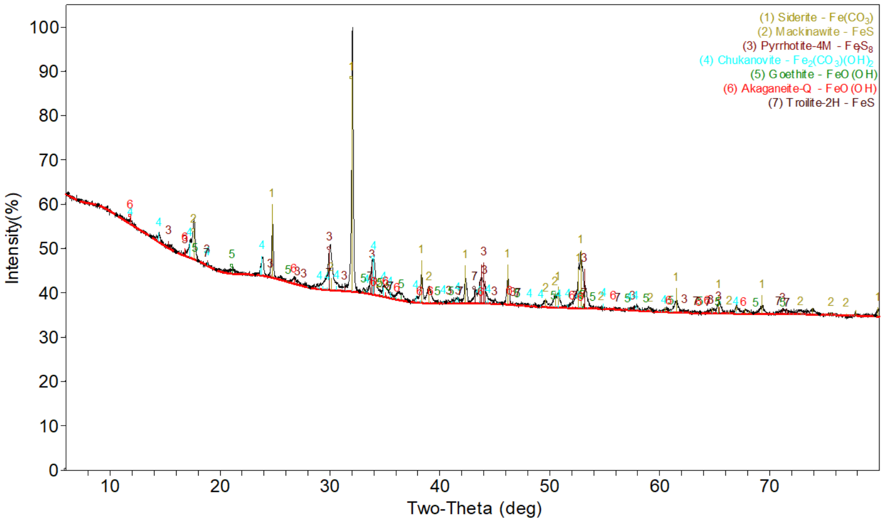

Figure 3a: Phase identification for sample 03.

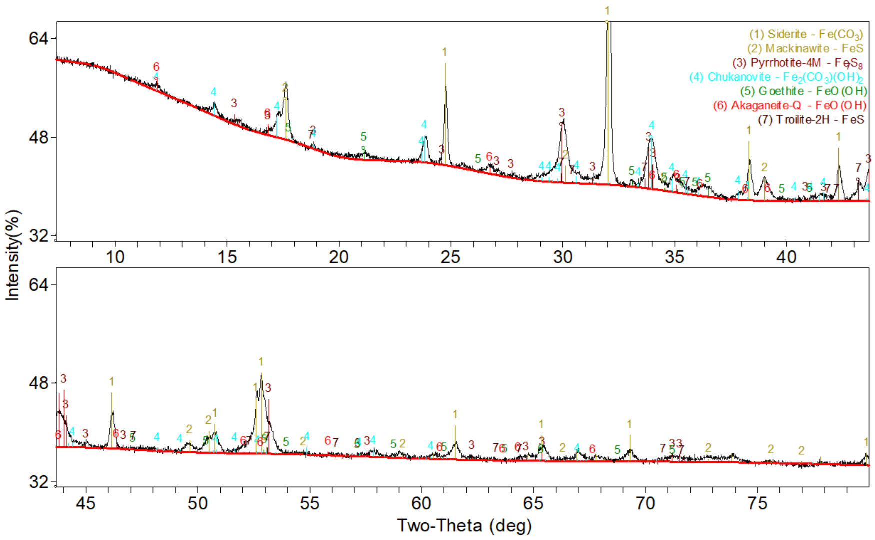

Figure 3b: Exploded view of phase identification for sample 03.

SUMMARY OF FINDINGS OF CASE STUDY 2

1. Iron-based corrosion deposits, such as $FeCO_3$ (Siderite), Fe_7S_8 (Pyrrhotite), $Fe_2(CO_3)(OH)_2$ (Chukanovite), FeS (Mackinawite), FeO(OH) (Goethite), FeS (Trollite), and FeO(OH,Cl) (Akaganeite), are commonly found in oil and gas wells. These deposits can form because of the interaction of formation fluids with iron-bearing minerals in the subsurface, or as a result of corrosion of iron-based equipment or well construction materials.
2. $FeCO_3$ (Siderite) is a mineral that is formed by the reaction of iron with carbon dioxide, which can occur in the presence of water. This mineral can be found in subsurface formations, but it can also form because of corrosion of iron-based equipment or well construction materials.
3. Fe_7S_8 (Pyrrhotite) and FeS (Mackinawite) are iron sulfides that can form because of the corrosion of iron-based alloys that are commonly used in well construction. The corrosion can happen due to the presence of sulfur compounds in the formation fluids or due to the presence of H_2S in the produced fluids.
4. $Fe_2(CO_3)(OH)_2$ (Chukanovite) is a mineral that is formed by the reaction of iron with carbon dioxide and water. This mineral can be found in subsurface formations, but it can also form as a result of corrosion of iron-based equipment or well construction materials.
5. FeS (Trollite) is a mineral that is formed by the reaction of iron with sulfur compounds. This mineral can be found in subsurface formations, but it can also form as a result of corrosion of iron-based equipment or well construction materials.
6. FeO(OH) (Goethite) is a mineral that is formed by the reaction of iron with oxygen and water. This mineral can be found in subsurface formations, but it can also form as a result of corrosion of iron-based equipment or well construction materials.
7. FeO(OH,Cl) (Akaganeite) is a mineral that is formed by the reaction of iron with oxygen, water, and chlorine. The presence of chlorine (Cl) in Akaganeite indicate that the well is operated in a saline environment, which can contribute to the formation of this mineral.

CASE HISTORY 3: CORROSION DEPOSITS COLLECTED AT A DEPTH OF 15442 FEET

XRD ANALYSIS OF DEPOSITS COLLECTED FROM A DIFFERENT WELL

The corrosion deposit was collected from a different well. The deposit was black in color and in paste form. There is no odor of rotten egg from the deposits. The XRD data is shown in Table 3 below, and the XRD spectrums are shown in Figure 4.

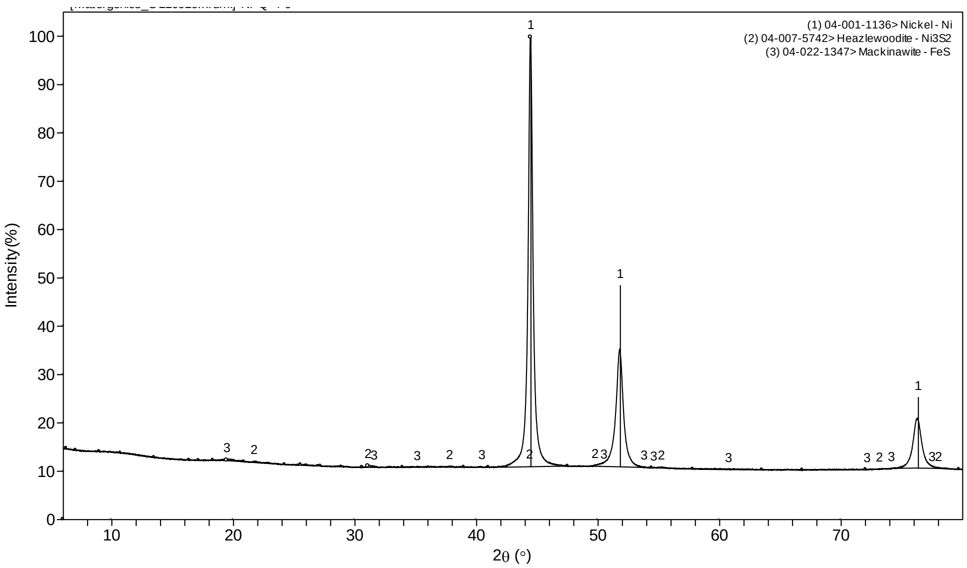

Figure 4a: Phase identification for sample 04.

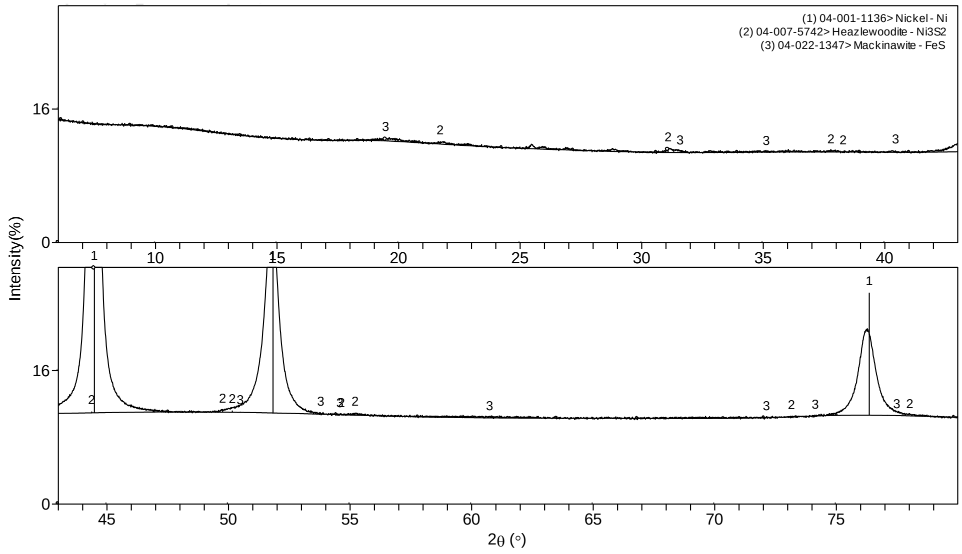

Figure 4b: Exploded view of phase identification for sample 04.

Table 3: Crystalline Phase Analysis (wt. %)

	Deposit collected at Depth: 15442 Ft (sample 4)
Ni (Nickel, FCC)	97.9
Ni_3S_2 (Hazelwoodite)	1.1
FeS (Mackinawite)	1.0

SUMMARY OF FINDINGS OF CASE STUDY 3

1. Ni (Nickel, FCC) is a metal that is commonly used in many types of alloys, including those used in well construction. Nickel alloys such as Inconel, Monel and Hastelloy are common in downhole applications, and they are resistant to corrosion in harsh environments such as high temperatures and high pressures. However, corrosion can still occur due to the presence of corrosive fluids, gases, or impurities in the well. The FCC stands for face-centered cubic and it is a term used to describe the crystal structure of the nickel.

   Nickel (Ni) concentration of 97.9% implies that the sample is predominantly composed of Nickel, which might suggest a few possibilities:

   a) **Material Composition**:
      - The equipment is made from nearly pure nickel or a nickel-rich alloy. While pure nickel is used in some applications, nickel alloys are more common in downhole conditions due to their enhanced properties.
      - Some nickel alloys used in the industry have a high nickel content. For example, Nickel 200/201 are commercially pure (99.6%) nickel materials.

   b) **Corrosion Products**:
      - High Ni concentration suggest that the corrosion is selectively leaching elements, leaving behind a nickel-enriched layer. This can happen in certain types of localized corrosion, like pitting or dealloying, where some components of the alloy are preferentially removed.

   c) **Alloy Degradation**:
      - In some harsh conditions, even resistant alloys can degrade over time. The presence of corrosive agents like hydrogen sulfide (H_2S), carbon dioxide (CO_2), chlorides, and high temperatures can lead to corrosion. If the corrosion mechanism involves selective leaching, it could leave behind an enriched layer of more corrosion-resistant material, in this case, nickel.

2. Ni_3S_2 (Hazelwoodite) is a mineral that is formed by the reaction of nickel with sulfur compounds. It can be a by-product of corrosion of nickel-based alloys. Specifically, the corrosion of nickel alloys in the presence of sulfur-containing compounds such as H_2S can lead to the formation of Ni_3S_2. This corrosion can happen in the wellbore, on the surface of the equipment, or in the reservoir.
3. FeS (Mackinawite) is an iron sulfide that can form as a result of the corrosion of iron-based alloys that are commonly used in well construction. The corrosion can happen due to the presence of sulfur compounds in the formation fluids or due to the presence of H_2S in the produced fluids. Specifically, the corrosion of iron alloys in the presence of sulfur-containing compounds such as H_2S can lead to the formation of FeS.

CASE HISTORY 4: CORROSION DEPOSITS COLLECTED FROM VARIOUS WELLS IN THE SAME BLOCK

The corrosion deposits were collected from various wells in the same block. They share same reservoir. While wells in the same block might share a reservoir, the complexity and heterogeneity of subsurface geology, along with operational differences, can lead to significant variations in scale deposits concentrations. The deposits were black in color and in paste form. There is no odor of rotten egg from the deposits. The XRD data is shown in the Table 4 below.

Table 4: Crystalline Phase Analysis (wt. %)

	Crystalline Phase Analysis (wt. %)						
	Well 1	**Well 2**	**Well 6**	**Well 7**	**Well 9**	**Well 10**	**Well 12**
$Ba(SO_4)$ (Baryte)	38.0	5.1	-	-	-	25.4	14.0
$Ca(CO_3)$ Aragonite	15.8	20.0	11.2	-	-	26.8	-
$CaMg(CO_3)_2$ (Dolomite)	12.2	6.3	-	-	-	-	18.5
$CaCO_3$ (Calcite)	10.1	20.7	-	27.9	-	-	45.1
$CaSO_4$ (Anhydrite)	9.5	44.8	71.4	59.4	57.4	42.6	13.0
SiO_2 (Quartz)	5.4	-	-	-	-	-	-
FeO(OH) (Lepidocrocite)	3.4	-	-	-	-	-	-
$KAl_2(AlSi_3O_{10})(F,OH)_2$ (Muscovite)	1.1	-	-	-	-	-	-
$Fe(CO_3)$ (Siderite)	0.8	-	-	-	-	-	-
W (Tungsten)	0.5	1.4	2.1	7.0	2.8	2.0	1.8
Fe_3O_4 Magnetite	-	1.8	-	-	-	-	-
WS_2 Tungstenite	-	-	2.4	-	0.7	1.9	-
$CuFeS_2$ (Chalcopyrite)	-	-	7.7	-	19.4	-	5.5
NaCl (Halite)	-	-	3.7	-	10.4	-	-
PbS (Galena)	-	-	1.5	5.7	3.5	1.3	1.9
FeS_2 (Pyrite)	-	-	-	-	5.7	-	0.3

SUMMARY OF FINDINGS OF CASE STUDY 4

The mineral composition in various oil wells often serves as an indicator of the subsurface geochemical processes. These compositions can give insights into the historical and ongoing interactions between reservoir fluids, hydrocarbons, and the formation rocks. In an oil production context, these minerals can influence production rates, reservoir quality, equipment longevity, and even overall profitability. Let's delve deeper into these minerals in relation to oil production:

1. **$Ba(SO_4)$ (Baryte)**: Predominantly found in Well 1, but also present in Wells 10 and 12.
    - **Formation**: Arises from the interaction of barium-rich formation waters with sulfate ions, possibly introduced by seawater breaches or formation water itself. $Ba^{2+}+SO_4^{2-} \rightarrow BaSO_4$
    - **Implications**: Baryte scales can drastically reduce reservoir permeability and can clog production equipment, leading to reduced oil flow. Effective scale inhibitors might be necessary to prevent its formation during production.
2. **$Ca(CO_3)$ (Aragonite and Calcite)**:
    - **Formation**: Indicates CO_2 interactions in the reservoir, which could be from gas zones, microbial degradation of organic matter, or from CO_2 injection in enhanced oil recovery processes. $Ca^{2+}+CO_3^{2-} \rightarrow CaCO_3$
    - **Implications**: Such scales can hinder oil flow by reducing permeability. Additionally, the release of CO_2 can lead to equipment corrosion.
3. **$CaMg(CO_3)_2$ (Dolomite)**:
    - **Formation**: Dolomite forms in the presence of magnesium-rich formation fluids, where magnesium partially replaces calcium in calcite structures. $CaCO_3+Mg^{2+} \rightarrow CaMg(CO_3)_2$
    - **Implications**: It may modify reservoir wettability, affecting oil mobility and extraction efficiency.
4. **$CaSO_4$ (Anhydrite)**:
    - **Formation**: Reflects interactions with sulfate-rich waters, possibly due to seawater intrusions or ancient evaporitic deposits. $Ca^{2+}+SO_4^{2-} \rightarrow CaSO_4$
    - **Implications**: Anhydrite scales can be particularly hard and challenging to remove, potentially leading to a decrease in production efficiency.

5. **SiO_2 (Quartz)**:
    - **Formation**: Its presence suggests a siliciclastic input or silica-rich fluid migration. $Si(OH)_4 \rightarrow SiO_2+2H_2O$
    - **Implications**: Quartz can indicate reservoir rock composition, affecting reservoir porosity and permeability.
6. **Fe-based minerals**:
    - **Formation**: Indicates iron-rich formation waters, or iron might be a byproduct of the corrosion of downhole equipment.
    - **Implications**: Iron precipitates can reduce oil flow, and certain iron-based minerals can be corrosive, further exacerbating equipment integrity issues.
7. **Tungsten-based minerals**:
    - **Formation**: They hint at unique geochemical zones.
    - **Implications**: While they might not directly affect oil flow, these minerals can be abrasive and could affect drilling decisions.
8. **$CuFeS_2$ (Chalcopyrite)**:
    - **Formation**: Reflective of hydrothermal deposits or certain ancient marine sedimentary environments.
    - **Implications**: Such zones may be harder to drill through due to increased rock hardness or could reflect zones of metallic mineralization.
9. **NaCl (Halite)**:
    - **Formation**: Indicates zones with historically high salinity or evaporitic processes. $Na^{+}+Cl^{-} \rightarrow NaCl$
    - **Implications**: High salinity can cause corrosion in production equipment and affect separation processes.
10. **Sulfide minerals**:
    - **Formation**: Indicates sulfur-rich reservoir conditions, which might have formed under anaerobic conditions with microbial sulfate reduction.

- **Implications**: These sulfides can lead to souring of the oil, requiring special treatments. They can also be corrosive to equipment.

Having a profound understanding of the mineralogical composition of each well is pivotal for the oil industry. Not only does it offer insights into the geological history and geochemical processes within the reservoir but also allows for tailored strategies in drilling, production, and reservoir management, ensuring maximum efficiency and longevity of the well operations.

CONCLUSIONS

1. Corrosion deposits in oil and gas wells are influenced by a myriad of factors ranging from geological formations, the chemical composition of the fluids in the well, equipment materials, to the well's operating conditions.
2. Both the inherent geology of the formations and external factors like the use of certain drilling fluids and equipment materials play pivotal roles in determining the mineralogical composition within wells.
3. Iron, nickel, and their derivatives are prominent elements in corrosion deposits, often arising from the interaction of formation fluids with respective materials, either naturally occurring or as part of well construction.
4. A profound understanding of the mineralogical composition provides invaluable insights into geochemical processes, reservoir history, and potential operational challenges.

RECOMMENDATIONS

1. **Monitoring and Analysis**: Continuous monitoring of the chemical composition of formation fluids is essential. This helps in early prediction of potential mineral build-ups and taking corrective measures.

   Drilling Phase:

   - Implement real-time monitoring systems to analyze drilling mud and cuttings as they return to the surface. These systems can provide instant feedback on the chemical composition of the formation fluids and solids.
   - It is also valuable to collect samples at key intervals for detailed laboratory analysis, including XRD. These intervals could be determined by depth milestones, geological formations, or any significant change in drilling conditions.

   Production Phase:

   - Employ online analyzers that continuously sample the production fluids (oil, gas, water) for their chemical composition. These analyzers can often provide real-time data on various scales and corrosion indicators.
   - Automated sampling systems can be used to collect formation water at regular intervals for laboratory analysis, which can provide a more comprehensive understanding of the chemical composition.
   - Implement flow assurance programs that utilize the data from continuous monitoring to anticipate and prevent issues such as hydrate formation, wax deposition, and scaling.

2. **Equipment Evaluation**: Regular inspections and timely replacement of equipment, especially those made from tungsten carbide, iron-based alloys, and nickel-based alloys, are crucial to mitigate excessive wear and corrosion.

3. **Drilling Fluid Review**: The choice of drilling fluids should be regularly reviewed and adjusted, considering their potential contribution to mineral deposits in the well.

4. **Adapt Reservoir Management Practices**: With insights into mineralogical compositions, reservoir management strategies should be adjusted. This can ensure enhanced extraction efficiency and longevity of operations.

5. **Corrosion Mitigation**: Implement proactive corrosion prevention measures, considering the type of minerals formed. This includes using corrosion-resistant materials and inhibitors based on the specific challenges identified in each well.

6. **Tailored Drilling Strategies**: Understanding the mineralogical composition aids in formulating effective drilling strategies, especially in geochemically unique zones, to prevent equipment damage and maintain operational efficiency.

7. **Training and Skill Enhancement**: Regular training sessions for the on-field staff about the implications of the identified minerals can help in early detection and management of potential challenges.

REFERENCES

1. Syed R. Zaidi and Husin Sitepu. Characterization of Corrosion Products in Oil and Gas Facilities using X-ray Powder Diffraction Method. NACE CORROSION 2011, Paper 11393.
2. Syed R. Zaidi. Application of X-ray Powder Diffraction Techniques in Identification of Unknown Materials Formed in. NACE CORROSION 2012, Paper 01292.