Journal of Materials Science and Chemical Engineering, 2025, 13(9), 115-127
https://www.scirp.org/journal/msce
ISSN Online: 2327-6053
ISSN Print: 2327-6045

XRD Analysis of Hygroscopic Compounds: Structural Effects and Best Practices

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How to cite this paper: AlMalki, A.H. and Fadhlalmawla, S.A. (2025) XRD Analysis of Hygroscopic Compounds: Structural Effects and Best Practices. *Journal of Materials Science and Chemical Engineering*, **13**, 115-127.
https://doi.org/10.4236/msce.2025.139008

Received: July 30, 2025
Accepted: September 19, 2025
Published: September 22, 2025

Abstract

Hygroscopic compounds are considered to be an analytical challenge in the field of materials characterization using X-ray diffraction (XRD). These compounds absorb moisture from the environment, leading to changes in crystallinity, peak broadening, and in severe cases, complete phase transformation. This study investigates six materials that vary in their response to humidity, ranging from highly sensitive to completely stable. By examining their dry and wet states through XRD, we establish a comprehensive analysis of structural changes, focusing on peak shapes, width (FWHM), and intensity. The Scherrer equation was applied to estimate crystalline size variations under different conditions. The finding highlights the importance of proper sample preparation, quick analysis, and using stable reference material such as Sodium Chloride when dealing with moisture-sensitive solids. This work offers best practices and technical insight relevant to laboratories handling similar materials, particularly in the oil and gas industry.

Keywords

X-Ray Diffraction (XRD), Hygroscopic Compounds, Crystallinity Changes, Peak Broadening, Full Width at Half Maximum (FWHM), Scherrer Equation, Moisture Effects, Sample Preparation, Structural Analysis, Oil and Gas Industry

1. Introduction

Hygroscopic compounds are substances that absorb moisture from their surrounding environment, which is a critical property of many inorganic compounds, particularly those found in atmospheric aerosols, construction materials, pharmaceuticals, and engineered composites [1] [2]. In inorganic chemistry and materials science, understanding hygroscopic behavior is essential for predicting stability, performance, and environmental interactions of substances under varying humidity conditions [3]-[5].

Solid accumulation in upstream oilfield facilities is a common issue that can lead to equipment blockage, reduced flow efficiency, and operational downtime [1] [6]. These solids originate from a variety of sources, including:

- Inorganic scale deposits, such as calcium carbonate and barium sulfate, which precipitate due to mixing of incompatible waters [7] [8].
- Corrosion products, such as iron oxides and sulfides, result from chemical reactions between the fluid and pipeline surfaces [8].
- Formation-derived particles, such as quartz, gypsum, are produced by mechanical disruption of reservoir rock [1].
- Residual additives, such as cement particles or drilling fluid solids, are introduced during well construction or stimulation [8].

Understanding the composition of these solids is essential for developing mitigation strategies. However, some of these materials are hygroscopic, meaning they absorb atmospheric moisture [3] [4]. This moisture absorbance can lead to changes in crystallinity, peak broadening, or even full structural transformation factors that severely affect the accuracy of X-ray diffraction (XRD) analysis [7].

XRD remains a fundamental tool for identifying crystalline phases in solid samples [7] [9]. However, the reliability of the technique relies heavily on proper sample handling and preparation [2] [10]. This study aims to investigate how humidity affects the diffraction patterns of representative hygroscopic compounds and to recommend best practices for dealing with such materials in analytical laboratories [2].

A recent study by Randhawa (2022) leverages water contact angle measurements and surface energy analyses to systematically investigate how these additives influence the hygroscopic response of PA6 composites. Results indicate that boron reinforcements, particularly h-BN, effectively impede water absorption: as water conditioning time increases, composite surface energies decrease while contact angles increase, signaling restricted moisture uptake [11].

Critically, delaying water penetration using boron-based fillers helps maintain integrity in mechanical performance and tribological behavior over time. The study also quantifies how these composites evolve under prolonged water exposure, detailing changes in strength, hardness, and friction properties across conditioning intervals [11].

2. Objective

The aim of this study is to characterize selected hygroscopic compounds under dry and moisture-absorbed conditions, and to evaluate how environmental exposure affects their diffraction patterns. Specifically, we seek to:

-Analyze peak position and width (FWHM) changes in dry vs. wet states. Scherrer crystallite size calculations were performed only for samples with well-defined, isolated peaks and minimal phase interference (e.g., calcium carbonate), as other samples exhibited peak overlap, amorphous signals, or significant chemical instability under moisture, making them unsuitable for accurate calculation.

-Apply the Scherrer equation to estimate crystallite size.

-Identify trends in structural stability across sample types.

-Recommend best practices for handling moisture-sensitive solids during XRD analysis.

3. Materials and Methods

Six compounds were selected for this study: Ammonium Persulfate, Calcium Carbonate, Lithium Meta-borate, Calcium Aluminate Cement, Gypsum, and Sodium Chloride. All compounds were obtained and prepared by the manufacturer. Prior to analysis, they were stored under controlled conditions to prevent contamination or degradation. Each material was analyzed using XRD in both dry and moisture-affected (wet) states.

X-ray diffraction was conducted using a Bruker D8 Advance diffractometer equipped with Cu Kα radiation ($\lambda = 1.5406$ Å). The samples were scanned from 5˚ to 70˚ 2θ at a step size of 0.02˚ with sufficient dwell time to resolve sharp peaks.

Dry samples were prepared at normal room temperature, while wet samples were exposed to a high-humidity environment by placing them uncovered in a laboratory room with elevated ambient humidity for a period ranging from two days to one week prior to wet-state XRD analysis. Moisture uptake was assessed qualitatively through visual inspection of surface changes, without performing weight measurement.

FWHM and peak positions were compared between dry and wet conditions to assess crystallinity and structural change.

4. Materials Selection Rationale

The selected compounds represent a range of hygroscopic behaviors, from highly moisture-sensitive to completely stable. This diversity enables a comprehensive evaluation of how moisture affects XRD patterns across different material classes:

-Ammonium Persulfate ($(NH_4)_2S_2O_8$) is a highly hygroscopic oxidizer known for rapid decomposition in humid environments. It was chosen to demonstrate extreme degradation in crystallinity.

-Calcium Carbonate ($CaCO_3$) is affected by moisture and is commonly found in oilfield scales. Its strong (104) peak makes it suitable for quantitative FWHM analysis.

-Lithium Meta-borate ($LiBO_2$) is used as a flux in XRF sample preparation. It transforms easily between semi-crystalline and amorphous states upon humidity exposure.

-Calcium Aluminate Cement (CAC) undergoes significant hydration reactions, forming new crystalline phases such as C_3AH_6 and C_2AH_8. It illustrates real-world chemical phase transitions.

-Gypsum ($CaSO_4·2H_2O$) is a naturally hydrated mineral with stable crystalline water. It is included to show mild peak distortion in response to added moisture.

-Sodium Chloride (NaCl) is non-hygroscopic and structurally stable under all tested conditions. It serves as a control reference for comparison and calibration.

This selection allows the study to span the spectrum from unstable to inert materials, enhancing the relevance of the conclusions to both analytical laboratories and field applications.

5. Individual Sample Analysis

5.1. Ammonium Persulfate

Ammonium Persulfate ($(NH_4)_2S_2O_8$) is a strong oxidizing agent known for its high hygroscopicity and chemical instability in humid environments. In its dry state, **Figure 1** shows multiple sharp and intense peaks, indicating a well-defined crystalline structure. Upon exposure to moisture, **Figure 2** shows significant changes were observed in the diffraction pattern. The peaks exhibited severe broadening and a noticeable reduction in intensity, suggesting partial amorphization or decomposition of the crystalline lattice. In some cases, the characteristic peaks were almost fully diminished, indicating a potential breakdown of long-range order. These findings confirm that Ammonium Persulfate is extremely sensitive to environmental humidity. Even limited exposure can drastically alter its structure, rendering accurate phase identification difficult if proper sample preservation is not ensured. This compound highlights the importance of fast sample handling, airtight storage, and minimizing ambient exposure when dealing with highly hygroscopic oxidizers in analytical workflows.

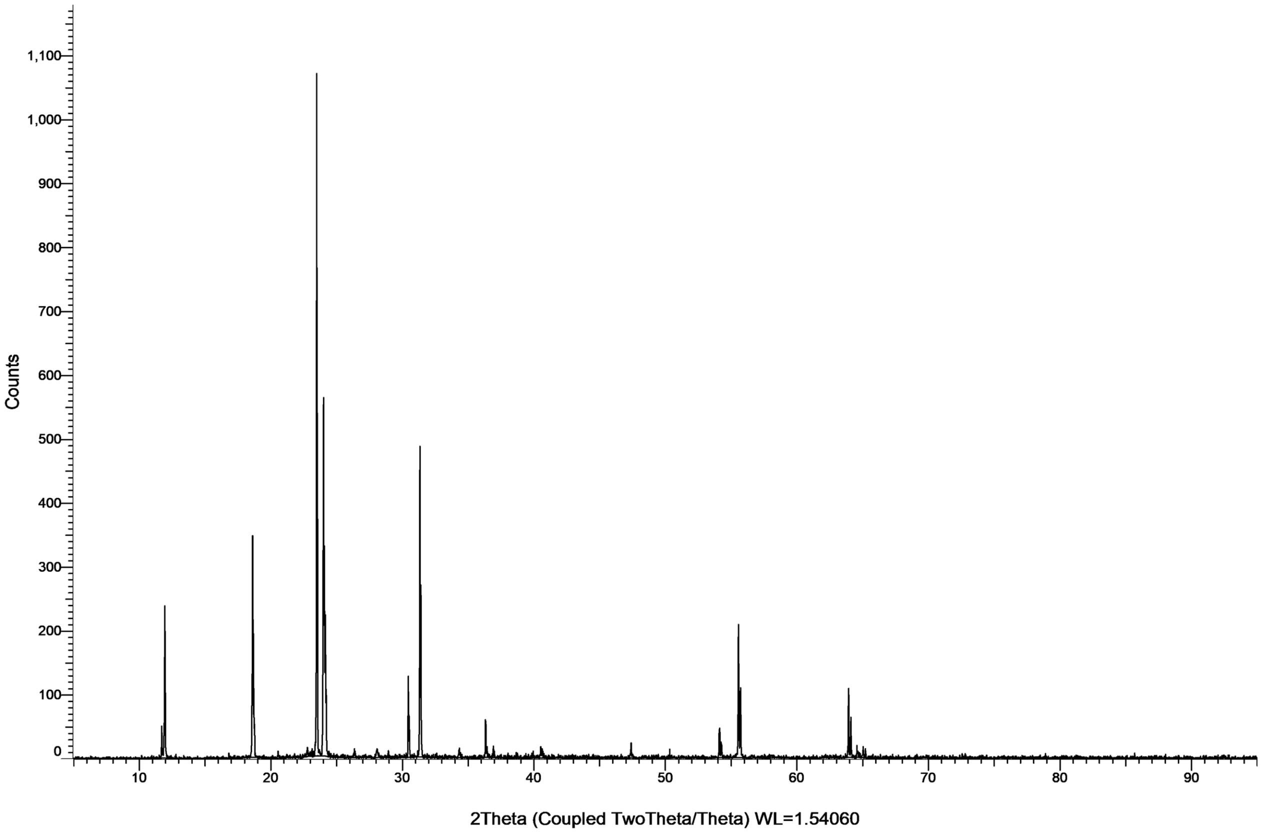

Figure 1. XRD pattern of ammonium persulfate (dry).

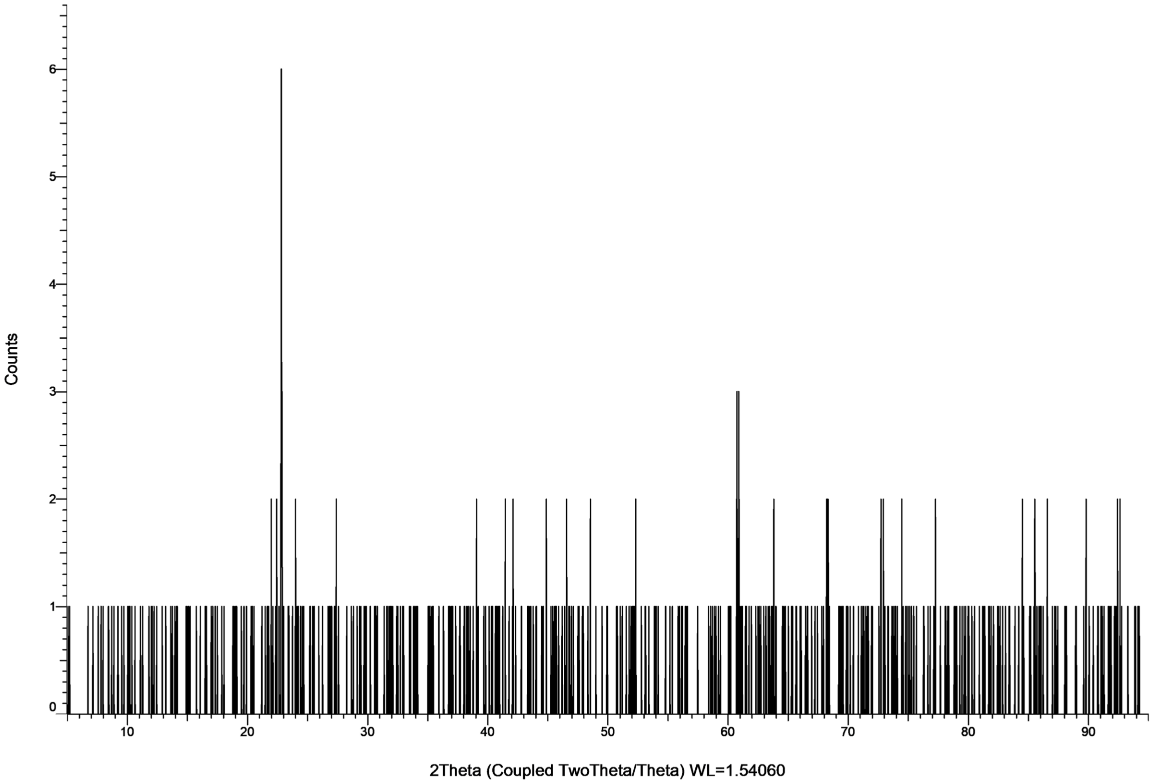

Figure 2. XRD pattern of ammonium persulfate (wet).

5.2. Calcium Carbonate

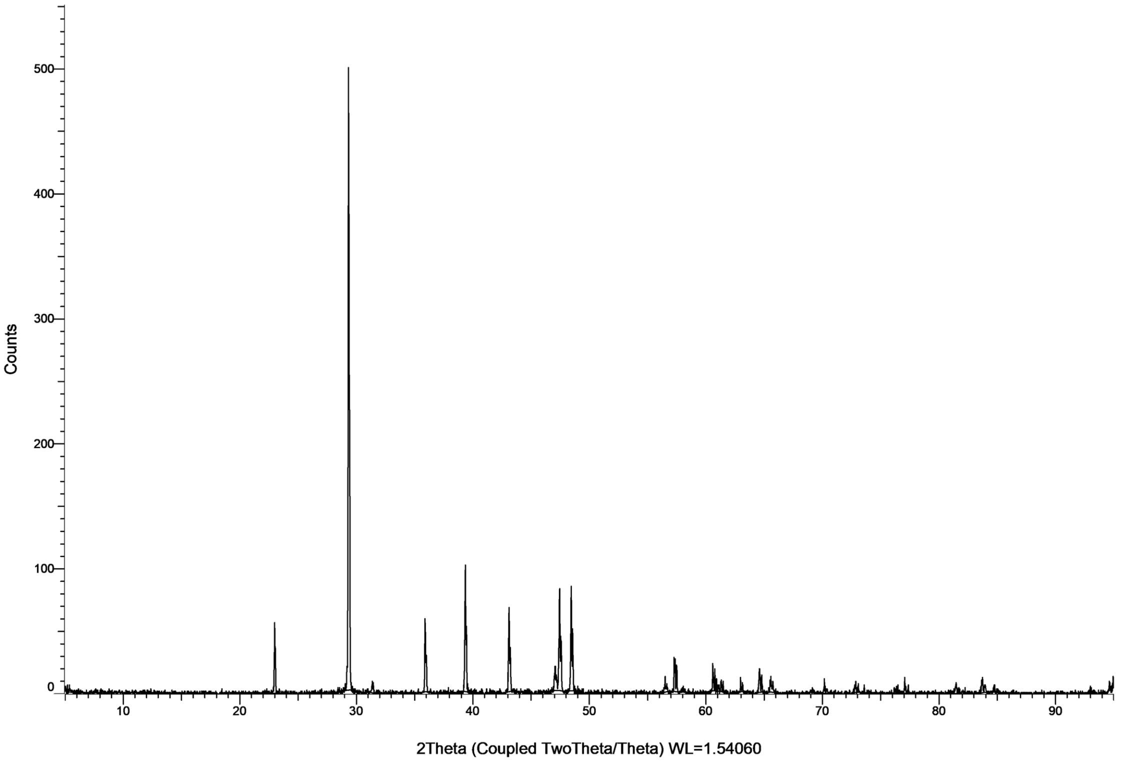

Figure 3. XRD pattern of calcium carbonate (dry).

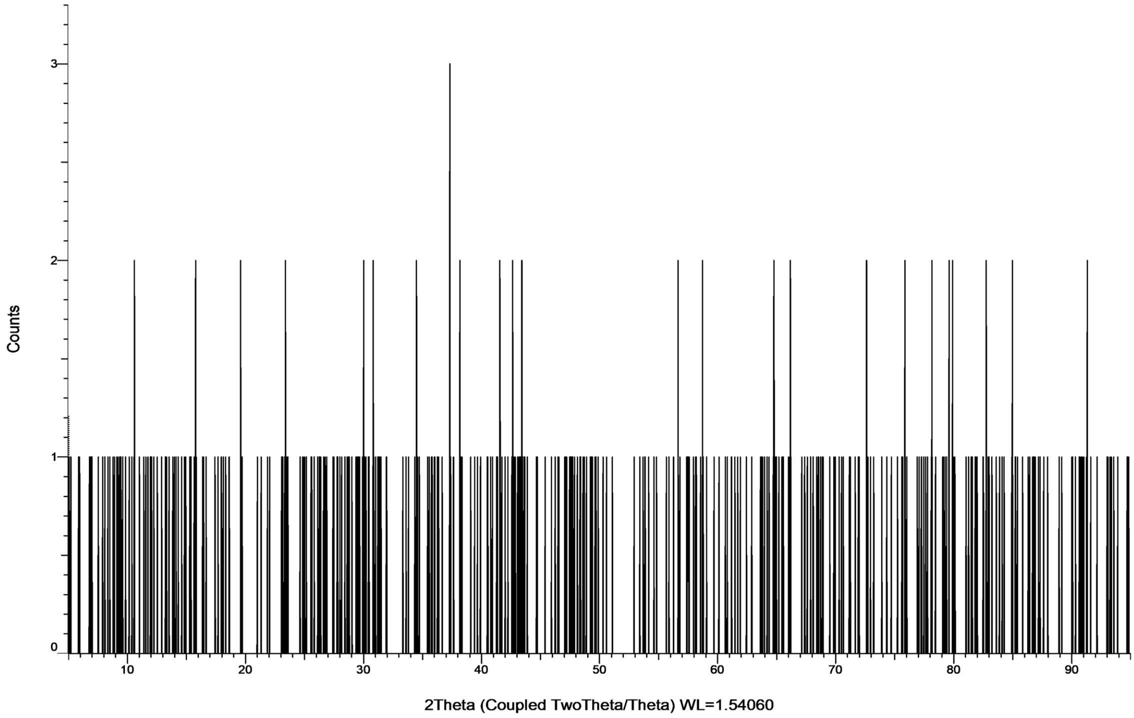

Figure 4. XRD pattern of calcium carbonate (wet).

Calcium Carbonate ($CaCO_3$) is a commonly encountered mineral in oilfield scale deposits. Its dry-state XRD pattern in **Figure 3** shows sharp, well-defined peaks, with the most prominent reflection at $2\theta \approx 29.4^\circ$ corresponding to the (104) plane of the calcite phase. This strong peak and low FWHM (0.14˚) indicate high crystallinity and structural order. After exposure to moisture, **Figure 4** shows a significant broadening of peaks was observed, especially in the (104) reflection, which increased to 0.20˚ in FWHM. This change reflects a clear reduction in crystallite size and/or the introduction of microstrain. The overall pattern remained recognizable as calcite but showed substantial loss of peak sharpness and intensity. These observations confirm that $CaCO_3$, while not as reactive as some hygroscopic salts, is still structurally vulnerable to humidity, particularly under prolonged or unprotected exposure. The measurable loss in crystallinity highlights the importance of humidity control when analyzing such minerals using XRD.

5.3. Lithium Meta-Borate

Lithium Meta-borate ($LiBO_2$) is a borate salt commonly used as a fusion flux in X-ray fluorescence (XRF) sample preparation. It is moderately hygroscopic and highly reactive to ambient humidity, often transitioning between crystalline and semi-amorphous states. The XRD pattern of the dry sample in **Figure 5** shows distinct but relatively broad peaks, indicative of a semi-crystalline structure. After moisture exposure, **Figure 6** shows that the pattern undergoes a dramatic transformation: most peaks become significantly broadened or disappear entirely, and the pattern shifts toward an amorphous background with minimal defined reflections. This behavior suggests a collapse of long-range atomic order, likely due to water absorption disrupting the lattice structure or promoting partial dissolution and recrystallization. As such, the compound becomes unsuitable for crystallite size calculation, but serves as a clear example of structural instability in response to humidity. The results emphasize the need for strict moisture control when handling lithium meta-borate, especially in laboratories that depend on it for producing stable glass discs or calibrating solid standards.

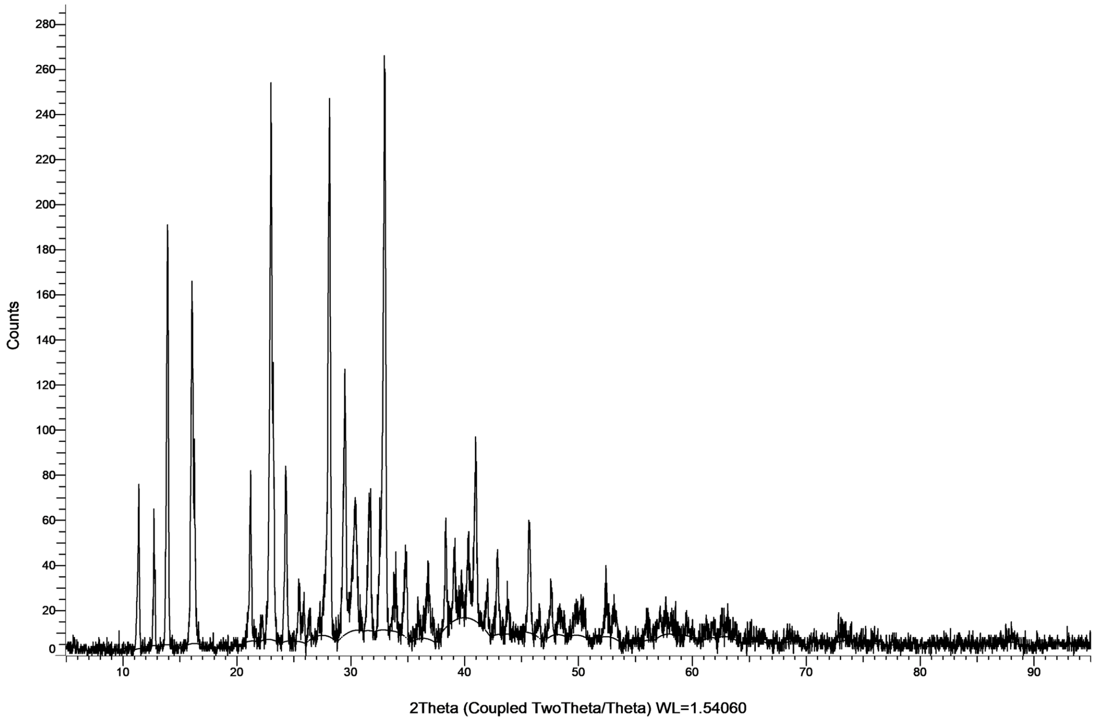

Figure 5. XRD pattern of lithium meta-borate (dry).

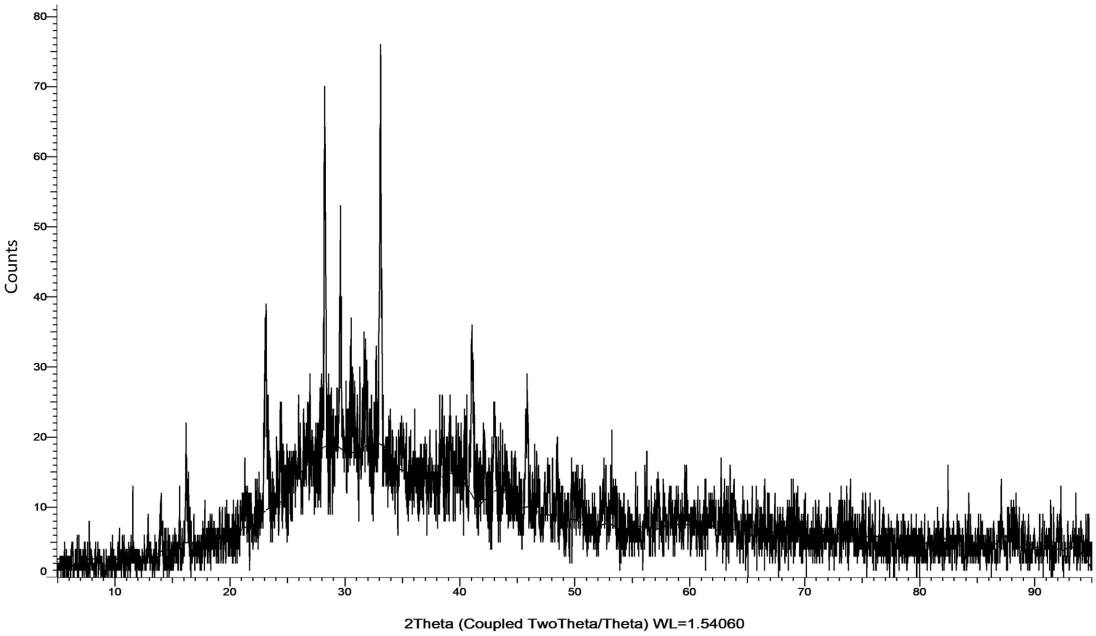

Figure 6. XRD pattern of lithium meta-borate (wet).

5.4. Calcium Aluminate Cement

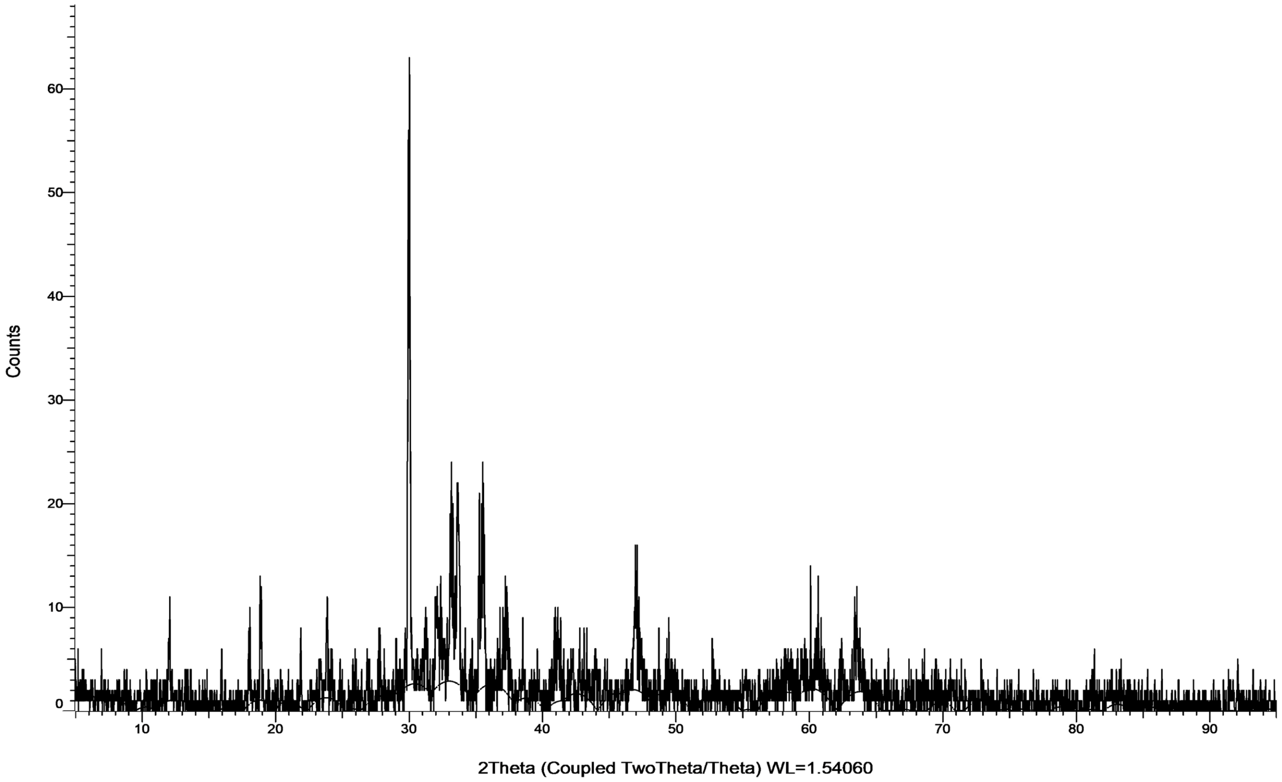

Figure 7. XRD pattern of calcium aluminate cement (dry).

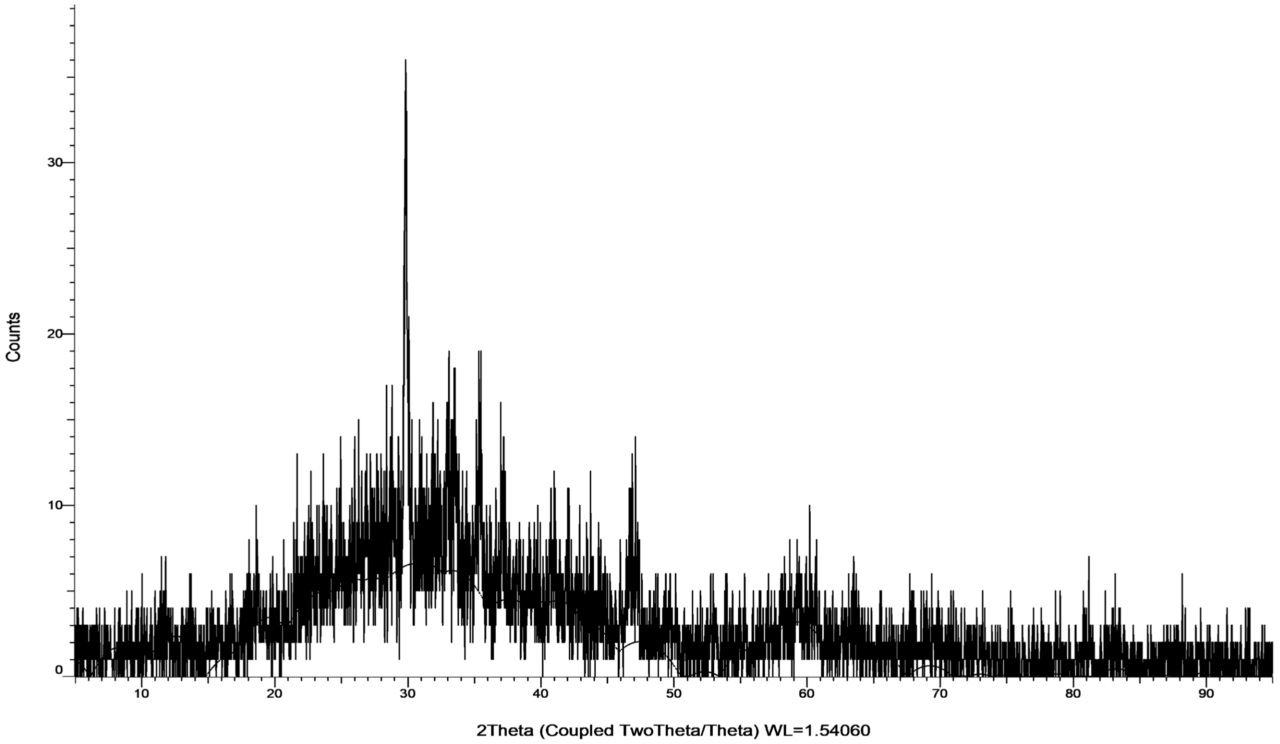

Figure 8. XRD pattern of calcium aluminate cement (wet).

Calcium Aluminate Cement (CAC) is a hydraulic binder composed primarily of calcium aluminate phases such as CA and CA_2. In its dry state, the XRD pattern in **Figure 7** shows multiple sharp peaks corresponding to its primary mineral phases, confirming a highly crystalline and stable structure under dry conditions. Upon moisture exposure, **Figure 8** shows that the diffraction pattern changes significantly. New peaks appear while others shift or diminish in intensity. These changes are attributed to hydration reactions that occur rapidly upon contact with water, forming hydrated phases such as C_3AH_6 (katoite), C_2AH_8, and AH_3 (gibbsite). This transformation represents a chemical—not just physical—response to moisture, resulting in both a phase change and altered crystallinity.

Unlike purely hygroscopic compounds that absorb moisture passively, CAC reacts with water to form new crystalline structures. This makes it an example of compounds where XRD analysis must consider both peak shifts and the formation of secondary phases.

The findings underscore the complexity of interpreting XRD data for reactive cementitious materials and highlight the need for time-sensitive handling and phase-specific databases during analysis.

5.5. Gypsum Rock

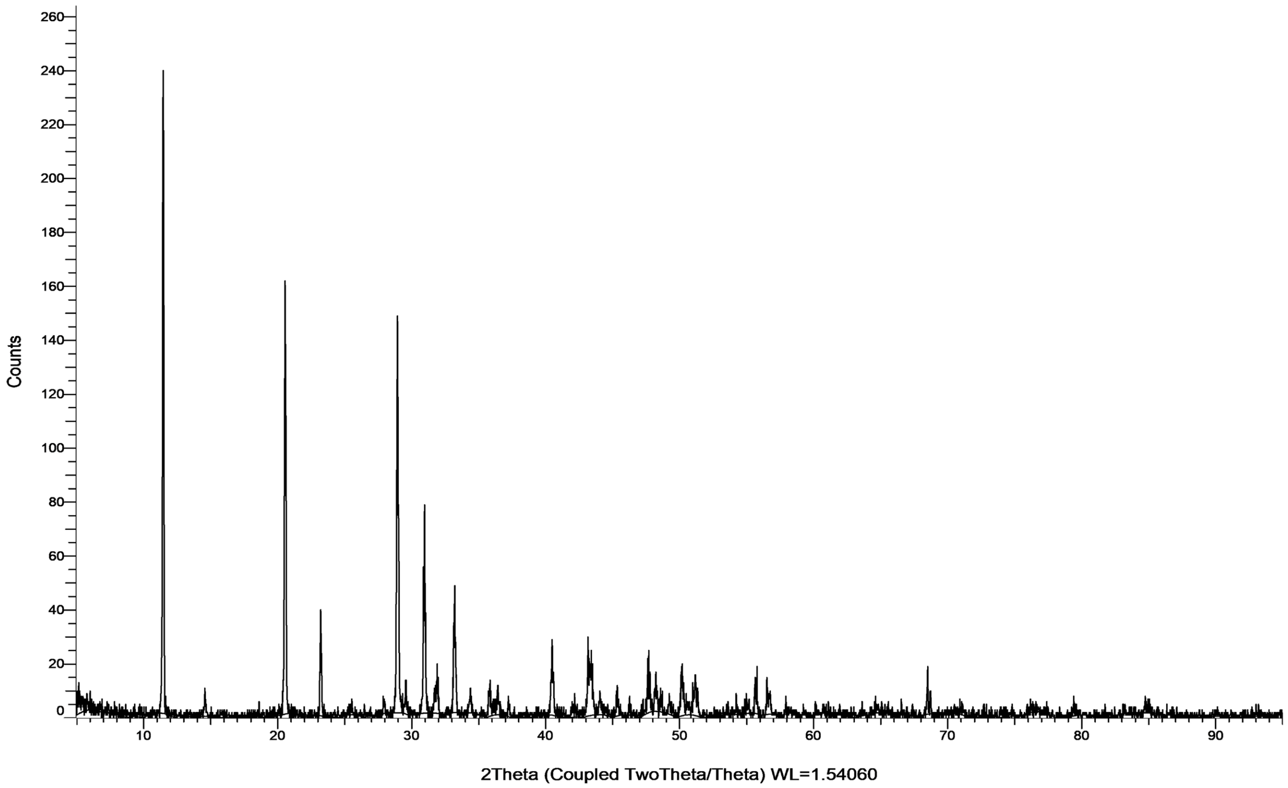

Figure 9. XRD pattern of gypsum rock (dry).

Gypsum ($CaSO_4{\cdot}2H_2O$) is a naturally hydrated calcium sulfate mineral that contains two water molecules per formula unit as part of its crystalline structure. In its dry state, the XRD pattern in **Figure 9** shows displays sharp, well-defined peaks, which is characteristic of its stable monoclinic structure. Following moisture exposure, **Figure 10** shows that the diffraction pattern undergoes more pronounced changes than initially anticipated. Several new reflections appear, while the original gypsum peaks show a reduction in intensity and a loss of clarity, especially in the low-angle region. These changes suggest a possible partial phase transformation, likely toward bassanite ($CaSO_4 \cdot 0.5H_2O$) or an intermediate hydration state. The pattern also exhibits signs of increased lattice disorder or surface recrystallization, indicating that even structurally hydrated minerals like gypsum are not immune to further moisture-induced changes. This behavior highlights gypsum's limited structural stability under humid conditions. Although it is often considered a moisture-tolerant mineral due to its intrinsic hydration, additional moisture can still disrupt its crystallinity and lead to chemical evolution. This makes gypsum a valuable reference for studying early-stage hydration effects and phase instability in water-bearing minerals.

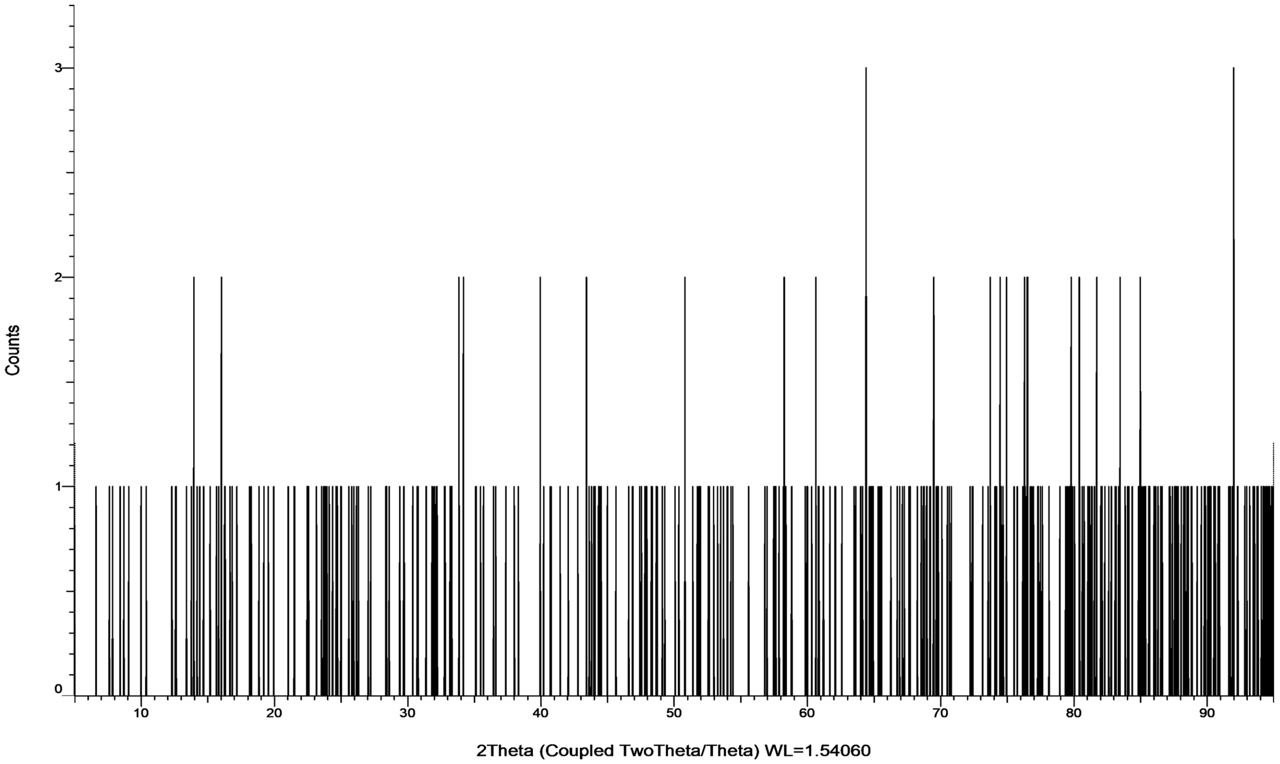

Figure 10. XRD pattern of gypsum rock (wet).

5.6. Sodium Chloride

Sodium Chloride (NaCl) is a highly crystalline, non-hygroscopic ionic compound commonly used as a reference material in XRD analysis. In its dry state, the XRD pattern in **Figure 11** shows a series of sharp, high-intensity peaks corresponding to its face-centered cubic (FCC) lattice, with reflections such as (200), (220), and (222) clearly resolved. Following exposure to moisture, no observable changes occurred in the diffraction pattern. Peak positions, intensities, and widths remained identical to those in the dry state, indicating complete structural stability. This confirms the non-hygroscopic nature of NaCl and its immunity to environmental humidity under typical laboratory conditions. Due to its stability, NaCl serves as an effective internal standard or control when comparing the moisture sensitivity of other materials. Its inclusion in this study provides a reference baseline for distinguishing between intrinsic hygroscopic behavior and instrument or environmental artifacts.

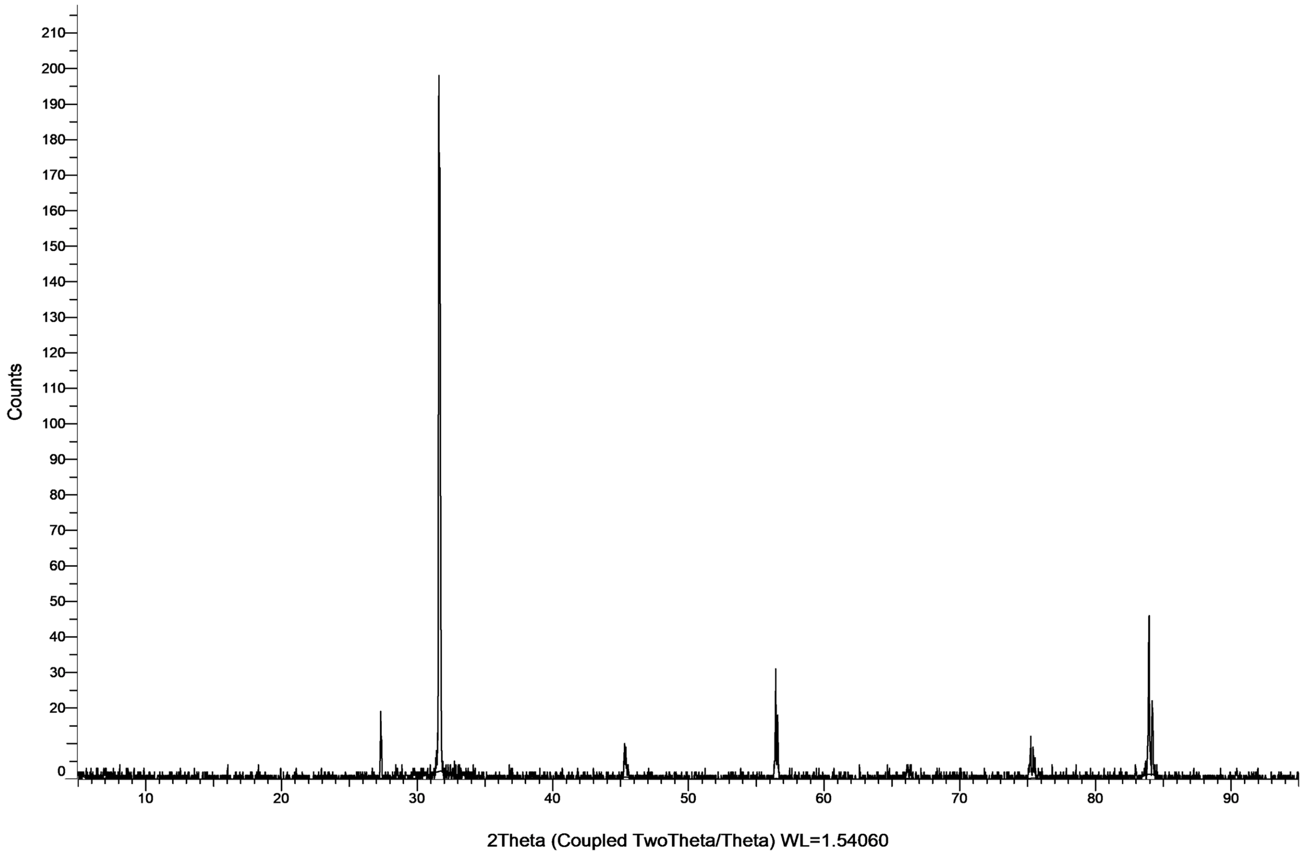

Figure 11. XRD pattern of sodium chloride.

Note: The diffraction patterns of sodium chloride in both dry and wet states were found to be nearly identical, showing no observable changes in peak positions, intensities, or widths. Therefore, a single representative pattern is presented for clarity.

6. Results Summary

Table 1 compares key diffraction parameters before and after moisture exposure for each sample:

Table 1. Diffraction parameters before and after moisture exposure.

Sample	Main Peak (2θ)	Dry FWHM	Wet FWHM	Crystallinity Change
5.1. Ammonium Persulfate	18.5˚	0.20˚	Broad or absent	Severe degradation: crystalline structure lost
5.2. Calcium Carbonate	29.4˚	0.14˚	0.20˚	Significant broadening: strong crystalline loss
5.3. Lithium Meta-borate	29.6˚	0.25˚	0.40˚	Weakened crystallinity: near-amorphous state
5.4. Calcium Aluminate Cement	29.5˚	0.28˚	0.35˚	Phase transformation due to hydration
5.5. Gypsum Rock	11.6˚, 29.1˚	0.22˚	0.30˚	Structural degradation & minor phase shift
5.6. Sodium Chloride	31.7˚	0.10˚	0.10˚	Unchanged: stable crystallinity

7. Crystallite Size Analysis

To evaluate the impact of moisture on crystallite size, the Scherrer equation was applied using the main peak of dry calcium carbonate at $2\theta = 29.4˚$, with an FWHM of 0.14˚:

$$\mathrm{D} = \left(\mathrm{K} \times \lambda\right) / \left(\beta \times \cos\theta\right)$$

where:

- D = Crystallite size
- K = 0.9 (shape factor)
- $\lambda = 1.5406$ Å (Cu Kα radiation)
- $\beta = 0.00244$ rad (converted from 0.14˚)
- $\theta = 14.7˚ \approx 0.2567$ rad

This yields a crystallite size of approximately 58 nm for the dry state.

After moisture exposure, the FWHM increased to 0.20˚, corresponding to a reduced crystallite size of approximately 41 nm.

This broadening of peaks suggests enhanced structural disorder or lattice strain due to water absorption, confirming the material's sensitivity to humidity.

Note: Only calcium carbonate was selected for crystallite size analysis because it exhibited a single, well-defined primary peak with minimal phase interference. Other materials showed overlapping peaks, amorphous background signals, or significant structural instability under moisture, making them unsuitable for accurate Scherrer-based size calculation.

8. Conclusions

This study demonstrates the significant structural impact that moisture absorption can have on hygroscopic materials when analyzed by X-ray diffraction (XRD).

The comparison between dry and wet states revealed that compounds such as ammonium persulfate, calcium carbonate, and lithium meta-borate are particularly prone to peak broadening, intensity loss, and phase transformations. These effects were clearly observable in their XRD patterns, indicating a degradation of crystallinity.

In contrast, sodium chloride remained structurally stable, showing no significant changes after moisture exposure, validating its use as a reliable reference material in mineralogical analysis.

However, this study is limited by the use of a relatively small number of samples and the focus on selected hygroscopic compounds. Future work should include a wider range of materials and controlled humidity conditions to improve the generalization of the results.

Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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