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Thermal Aging Assessment of Photovoltaic Cable Insulation Using XRF Spectroscopy

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Abstract.

The increasing deployment of photovoltaic systems requires reliable cable infrastructure capable of withstanding long-term thermal and environmental stresses. Polymeric insulation materials used in photovoltaic cables are susceptible to thermal degradation, which can progressively deteriorate their mechanical and dielectric properties. A key degradation mechanism of polyvinyl chloride insulation is dehydrochlorination, which leads to chlorine loss and structural changes in the polymer matrix. This paper investigates the applicability of portable energy-dispersive X-ray fluorescence spectroscopy as a non-destructive method for assessing thermal aging of photovoltaic cable insulation. Special attention is given to multilayer insulation, as the analyzed photovoltaic cable comprises two distinct layers (an inner white layer and an outer black layer) that may differ in composition and thermal response. Cable samples were subjected to controlled thermal exposure ranging from room temperature to 150 °C, covering both typical operating conditions and accelerated aging scenarios. Elemental analysis focused on monitoring chlorine content as the primary indicator of degradation. The results reveal a temperature-dependent decrease in chlorine content, with moderate changes up to 110 °C and a more pronounced decline above approximately 130 °C, indicating the onset of accelerated degradation. The findings confirm that portable X-ray fluorescence spectroscopy enables rapid, non-destructive evaluation of insulation condition, although careful interpretation is required for complex multilayer cable systems.

Key words. photovoltaic systems, cable insulation aging, polyvinyl chloride degradation, portable X-ray fluorescence spectroscopy, thermal reliability.

1. Introduction

The rapid growth of photovoltaic (PV) systems has led to an increasing demand for reliable and durable cable infrastructure. PV cables operate under challenging conditions, including elevated temperatures, solar radiation, and fluctuating electrical loads, which can significantly affect the long-term performance of their insulation materials.

Polymeric materials, particularly polyvinyl chloride (PVC), are widely used in cable insulation due to their favorable electrical properties, mechanical flexibility, and cost-effectiveness. However, PVC is known to degrade thermally when exposed to elevated temperatures for extended periods. One of the primary degradation mechanisms is dehydrochlorination, a process in which hydrogen chloride (HCl) is released from the polymer chain, reducing chlorine content and forming conjugated double bonds. This process not only alters the chemical composition of the material but also negatively impacts its dielectric strength and mechanical integrity. Traditional methods for evaluating cable insulation aging often involve destructive testing or require complex laboratory procedures. In contrast, X-ray fluorescence (XRF) spectroscopy offers a non-destructive and rapid alternative for elemental analysis. Portable XRF analyzers enable in situ measurements and have the potential to serve as diagnostic tools for assessing cable insulation condition in practical applications. Despite its advantages, the application of XRF for polymer degradation analysis presents certain challenges, particularly due to material heterogeneity and limitations in detecting light elements. In PV cables, the insulation often consists of multiple layers with different compositions, which can affect measurement accuracy and data interpretation.

The aim of this paper is to evaluate the potential of portable XRF spectroscopy for detecting thermal degradation in PV cable insulation. The analysis focuses on changes in chlorine content as a key indicator of degradation. Additionally, the paper considers the influence of the multilayer insulation structure and compares the behavior of PV cable insulation with that of conventional cable materials under controlled thermal conditions.

2. Experimental Procedure

A. Preparation of Insulation Material

The cable samples were prepared using two different approaches depending on the type of insulation analyzed. First, the polymer insulation was mechanically separated from the metallic conductor.

For conventional cable insulation, the material was mechanically crushed and ground to a fine powder to obtain a homogeneous sample. This approach reduces the influence of local material inhomogeneities and enables a more representative analysis of the average chemical composition. The analyzed PV cable features a multilayer insulation system comprising an inner (white) and an outer (black) layer, each with distinct composition and function. To preserve the true structure of the insulation system, the PV samples were not ground but analyzed in their original form. The samples were mechanically prepared to achieve a flat, compact surface, ensuring stable contact with the XRF analyzer and improving measurement repeatability. Prior to measurement, all sample surfaces were thoroughly cleaned with alcohol to remove possible contaminants and minimize their influence on the measurement results.

The preparation of insulation samples for thermal treatment and subsequent XRF analysis is shown in Fig. 1.

Fig. 1. Samples for thermal treatment and XRF analysis

B. Thermal Treatment of Samples

The prepared insulation samples were subjected to controlled thermal treatment in a laboratory temperature chamber, as shown in Fig. 2.

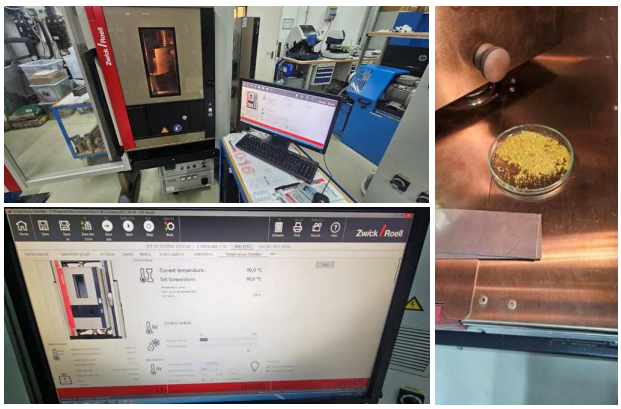

Fig. 2. Thermal treatment of insulation samples in a laboratory temperature chamber, including sample placement, heating environment, and temperature control interface

Each sample was exposed to a constant temperature for approximately 1.5 hours. The selected temperature levels were room temperature (reference sample), 50 °C, 70 °C, 90 °C, 110 °C, 130 °C, and 150 °C. This temperature range was chosen to represent both typical operating conditions and accelerated-aging scenarios for PV cables.

The temperature chamber provides precise temperature control and uniform heating conditions, ensuring repeatable experimental results. The samples were arranged in the chamber to ensure homogeneous exposure to the thermal field. Temperature was monitored and controlled using a digital system, allowing stable conditions throughout the entire exposure period. The thermal treatment was performed without additional mechanical or chemical influences, ensuring that the observed changes in chemical composition were primarily due to thermal degradation. After thermal exposure, all samples were cooled to room temperature under controlled conditions to prevent additional uncontrolled changes in material properties.

C. Pellet Preparation

After cooling, the thermally treated samples of conventional cable insulation were re-homogenized and pressed into compact pellets using a laboratory press. No binding agents were used, while uniform density and a smooth measurement surface were ensured.
Pellet preparation offers several advantages for XRF analysis:

- reduction of surface topography effects,
- improved measurement geometry stability,
- enhanced repeatability of results,
- reduction of matrix effects.

This approach is particularly important when analyzing heterogeneous materials, where local irregularities may significantly influence the measured values. In contrast, PV cable insulation samples were not pelletized, as the aim was to preserve the real multilayer structure and evaluate degradation under conditions closer to actual operation.

D. XRF Analysis

Elemental analysis of the insulation samples was performed using a portable energy-dispersive XRF analyzer (Niton XL3t GOLDD+). Measurements were carried out using a portable test stand (PTS), which ensured stable sample positioning and improved measurement repeatability. The experimental setup is shown in Fig. 3.

Fig. 3. Portable XRF analyzer (Niton XL3t GOLDD+) with PTS measurement stand used for stable and repeatable analysis of insulation samples

A measurement protocol optimized for polymer materials was used, focusing on the detection of halogens, particularly chlorine, and stabilizing elements such as calcium (Ca) and zinc (Zn), in accordance with the principles of quantitative XRF spectrometry.

For conventional cable insulation, measurements were performed on homogenized samples in pellet form, allowing representative evaluation of the average chemical composition. In contrast, PV cable insulation was measured directly on non-homogenized multilayer samples, with measurements performed at the sample surface. For each sample, three consecutive measurements were performed, and the average was calculated. This approach reduces the influence of random deviations and increases the reliability of the results. Repeated measurements also enable evaluation of result variability, which is particularly important for heterogeneous multilayer materials. This allows distinguishing between actual chemical changes and measurement-related variations. Examples of XRF measurement results for thermally treated insulation samples are shown in Fig. 4 and Fig. 5.

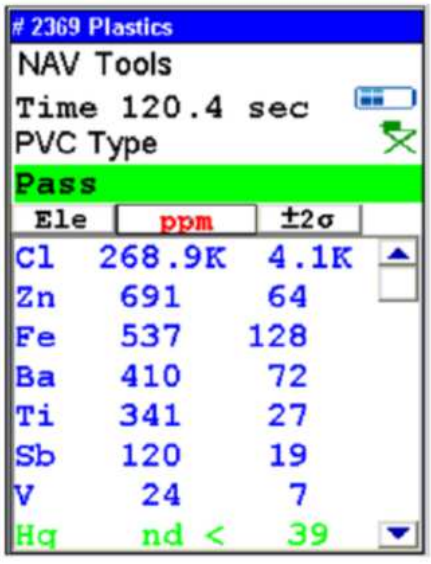

Fig. 4. Measurement results of insulation at 90 °C

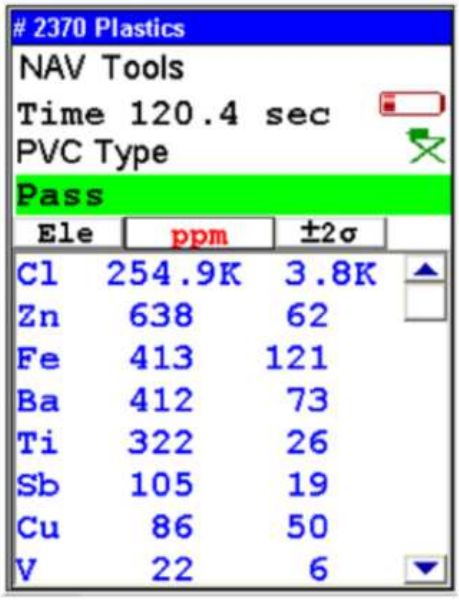

Fig. 5. Measurement results of insulation at 110 °C

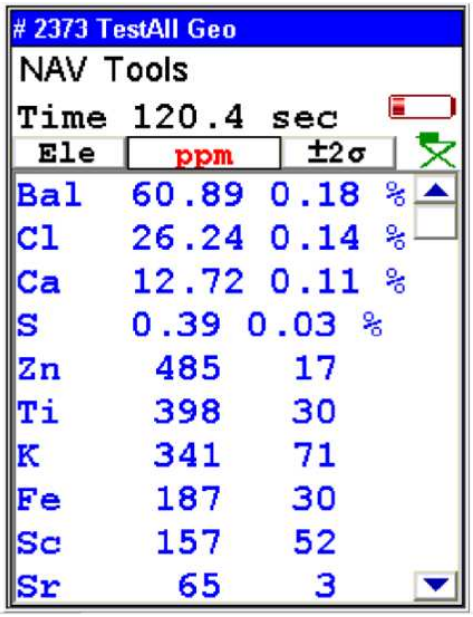

Fig. 6. Example of XRF measurement using TestAll Geo mode showing elemental composition of PVC insulation sample

In addition, selecting appropriate measurement parameters is crucial for obtaining reliable XRF results. Parameters such as measurement time, excitation conditions, and detector settings directly influence the signal-to-noise ratio and detection limits. In this paper, measurement conditions were selected to ensure sufficient counting statistics while maintaining reasonable analysis time, making the method suitable for both laboratory and potential field applications.

Furthermore, matrix effects and sample density may influence the measured intensities, particularly in heterogeneous polymer materials. The use of a measurement stand (PTS) and consistent sample positioning minimizes such effects and improves repeatability. These considerations are essential for

obtaining reliable quantitative results when applying portable XRF to polymer-based insulation systems.

E. Comparison of XRF Measurement Modes

In addition to the polymer-specific measurement mode (Plastics), comparative measurements were also performed using the TestAll Geo protocol.

The TestAll Geo protocol is intended for general elemental analysis of materials, primarily geological samples, and enables the detection of a broader range of elements expressed in mass fractions. An example of measurement results obtained using this protocol is shown in Fig. 6, where a broader elemental composition of the sample, including Ca, K, Ti, and Fe, is observed, along with the chlorine content expressed as mass percentages. However, because calibration specifically adapted to polymer materials is unavailable, this measurement mode does not provide optimally accurate quantification for PVC insulation. In contrast, the Plastics protocol is specifically optimized for polymer materials, particularly PVC, and enables more accurate quantification of halogens, especially chlorine, as well as stabilizing elements such as Ca and Zn. Owing to calibration tailored to the polymer matrix, this mode provides more reliable, repeatable results for evaluating insulation degradation.
Therefore, all results presented in the Results and Discussion section are based on measurements performed using the Plastics mode, whereas TestAll Geo was used only for comparative and illustrative purposes.

3. Results and Discussion

All presented results are based on measurements performed using the Plastics mode, which is optimized for polymer analysis and provides more reliable quantification of chlorine content. The results of the XRF analysis show clear temperature-dependent changes in the chemical composition of PVC insulation material. The main focus of the analysis was monitoring chlorine (Cl) content, a key indicator of thermal degradation associated with the dehydrochlorination process.

A. Effect of temperature on chlorine content

Table 1 presents the average values of selected elements (Cl, Ca, Zn) at different thermal treatment temperatures. Chlorine is expressed as a mass percentage, while calcium and zinc are expressed as ppm.

Table 1. Average elemental composition of PVC insulation.

T (°C)	Cl (%)	Ca (ppm)	Zn (ppm)
70	26.9	1820	489
90	26.3	1795	492
110	25.6	1770	487
130	24.1	1740	483
150	22.3	1705	488

The results show a gradual decrease in chlorine content with increasing temperature. Up to approximately 110 °C, the changes are relatively moderate, indicating the early stages of material degradation. In this temperature range, initial chemical processes dominate and do not yet cause significant structural changes in the material.

At higher temperatures (130–150 °C), a more pronounced decrease in chlorine content is observed, indicating the transition to an accelerated degradation phase. This behavior is characteristic of the dehydrochlorination process, in which hydrogen chloride (HCl) is released from the polymer chain. As a result, conjugated double bonds form, further destabilizing the polymer structure.
Fig. 7 illustrates the variation of chlorine content as a function of temperature. A clear decreasing trend is observed, confirming the temperature dependence of the degradation process and indicating a transition region around 130 °C, where the degradation rate significantly increases.

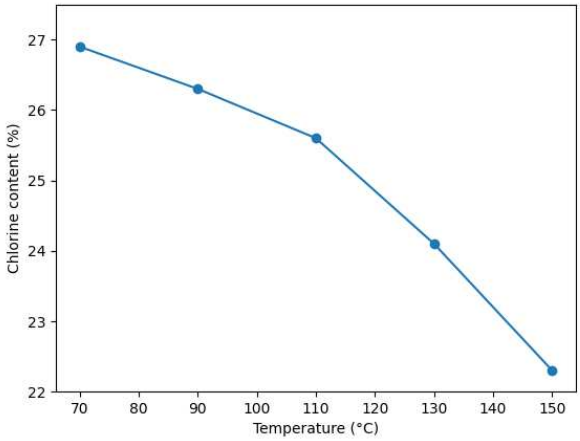

Fig. 7. Variation of chlorine content in PVC insulation as a function of temperature

The temperature-dependent decrease in chlorine content also suggests the potential to identify characteristic degradation temperature thresholds. The transition region around 130 °C, where the slope of the curve changes significantly, can be interpreted as the boundary between the initial and accelerated phases of PVC degradation. Such information is highly relevant from a practical perspective, as it enables a more accurate assessment of critical operating conditions under which faster insulation degradation may occur. In the context of PV system operation, this implies that prolonged exposure to temperatures above this threshold can significantly affect the service life of cable infrastructure. The identification of such thresholds using non-destructive methods, such as XRF, represents an important step toward the development of advanced diagnostic approaches based on the actual condition of the material (condition-based monitoring), rather than relying solely on time-based maintenance intervals.

B. Relative changes of elements

Fig. 8 presents the relative changes of selected elements (Cl, Ca, Zn) in PVC insulation after thermal treatment at different temperatures, normalized to the reference condition.

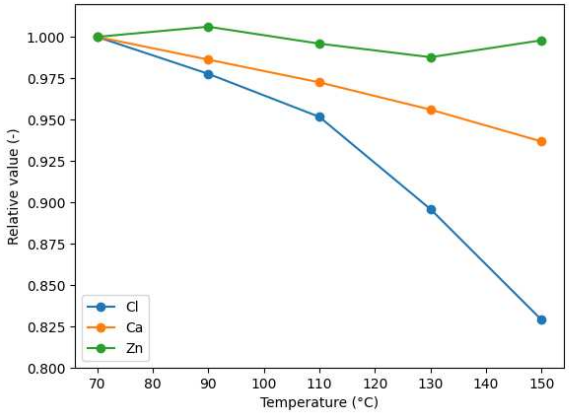

Fig. 8. Relative changes of Cl, Ca and Zn in PVC insulation as a function of temperature

While chlorine content shows a pronounced sharp increase with increasing temperature, changes in stabilizing elements such as calcium and zinc are less pronounced. Calcium exhibits a slight decreasing trend, which may be associated with redistribution of stabilizers or local changes in the chemical structure of the material. In contrast, zinc remains nearly constant, further confirming the relative stability of metallic additives compared to the polymer matrix.

The results clearly confirm that the dominant degradation process is chlorine elimination from the polymer matrix, while metallic stabilizers remain largely unaffected. Minor deviations observed for Zn are within the measurement uncertainty. It is also important to note that the relatively stable behavior of calcium and zinc suggests that the degradation process is predominantly governed by changes in the polymer matrix rather than by the depletion of stabilizing additives. This observation is consistent with the role of Ca/Zn stabilizers, which primarily act to delay degradation processes rather than being consumed in early degradation stages. Their stability further supports the interpretation that chlorine loss remains the most reliable and sensitive indicator of thermal aging in PVC insulation.

C. Changes in stabilizing elements

In addition to chlorine, calcium (Ca) and zinc (Zn), which are commonly used as stabilizers in PVC materials, were also analyzed. Their primary role is to inhibit degradation processes, particularly dehydrochlorination.

The results indicate that the concentrations of these elements do not change significantly with temperature, suggesting that stabilizers remain relatively stable within the investigated temperature range. This confirms that the primary degradation mechanism involves the breakdown of the polymer structure rather than the decomposition of additives.

D. Interpretation of the degradation mechanism

The decrease in chlorine content is directly related to the dehydrochlorination process, which represents the key mechanism of thermal degradation of PVC. During this process, HCl is released from the polymer chain, leading to the formation of conjugated structures and changes in the chemical composition of the material.
These chemical changes are also reflected in the physical properties of the material, such as:

- discoloration (yellowing and darkening),
- increased brittleness,
- reduced mechanical strength,
- deterioration of dielectric properties,
- increased risk of electrical breakdown.

Although XRF does not directly measure mechanical or electrical properties, it enables monitoring of key chemical indicators of degradation, representing a significant advantage in non-destructive diagnostics.

E. Influence of multilayer structure and comparison with conventional cable

To improve the interpretation of the results, a comparison with conventional cable insulation, which represents a more homogeneous system, was conducted.

In the case of conventional cable insulation, where samples were homogenized and analyzed as pellets, a more pronounced, monotonic decrease in chlorine content with increasing temperature was observed. In contrast, PV cable insulation, which consists of a multilayer structure (inner white and outer black layer), does not always exhibit a perfectly linear trend. This behavior can be attributed to material heterogeneity and different exposure conditions of individual layers. The outer layer is directly exposed to environmental influences and higher temperatures, while the inner layer is in contact with the conductor, which may introduce local temperature gradients. As a result, degradation does not occur uniformly across the insulation cross-section, leading to increased variability of measurement results.

This behavior underscores the importance of accounting for spatial variability when analyzing multilayer insulation systems. A single-point measurement may not fully represent the overall degradation state, particularly in real cable applications where degradation is not uniformly distributed across the insulation thickness.

Localized degradation phenomena may therefore remain undetected, which emphasizes the need for multiple measurements or scanning approaches when assessing real cable systems. This aspect is particularly relevant for in situ diagnostics, where access to internal layers is limited, and measurements are typically performed on the external surface.

F. Applicability of the XRF method for diagnostics

The obtained results confirm that portable XRF spectroscopy is a suitable method for monitoring thermal degradation of PVC insulation. The method enables:

- rapid and non-destructive analysis,

- minimal sample preparation,
- potential for field application,
- detection of early chemical changes.

However, careful interpretation of results is required, particularly for multilayer systems, where degradation is not necessarily homogeneous. It is therefore recommended to perform multiple measurements at different locations or to combine XRF with complementary methods to obtain a more representative assessment.

G. Limitations and measurement uncertainty

Although the presented results clearly show temperature-dependent degradation trends, several factors may affect the accuracy and repeatability of XRF measurements. One key limitation is the heterogeneous nature of PV cable insulation. Since measurements were performed directly on non-homogenized multilayer samples, local variations in composition and structure may contribute to increased data dispersion.

Additionally, XRF analysis is sensitive to surface condition and measurement geometry. Despite careful cleaning and preparation, small differences in surface roughness or positioning may influence the detected signal. Another important limitation is the inability of XRF to detect light elements, particularly carbon, which represents a significant fraction of polymer materials. Therefore, the analysis focuses on chlorine and selected metallic elements as indirect indicators of degradation.

Finally, differences between measurement protocols (TestAll Geo vs. Plastics) further highlight the importance of appropriate calibration, as improper selection may lead to systematic deviations in quantitative results.

4. Conclusion

This paper investigated the applicability of portable energy-dispersive XRF spectroscopy for assessing the thermal aging of PVC insulation in PV cables. The results revealed a clear, temperature-dependent decrease in chlorine content, with a more pronounced decline above approximately 130 °C, indicating a transition to an accelerated degradation phase. This behavior is consistent with the dehydrochlorination mechanism and confirms chlorine content as a reliable indicator of thermal degradation in PVC materials.

The comparison with conventional cable insulation showed that the multilayer structure of PV cables leads to a more complex, non-uniform degradation process. Variations in exposure conditions across individual layers increase measurement variability and highlight the importance of careful interpretation. The findings confirm that portable XRF spectroscopy represents an effective, rapid, and non-destructive method for evaluating the condition of cable insulation, with strong potential for field applications. The method enables the detection of early chemical changes associated with material degradation and supports the development of advanced diagnostic approaches.

However, certain limitations should be considered, including the heterogeneous nature of multilayer insulation systems, sensitivity to surface conditions, and the inability to detect light elements such as carbon. Future research will focus on long-term aging effects and on integrating complementary methods to enable a more comprehensive evaluation of mechanical and electrical properties.

The results also demonstrate the potential of portable XRF as a screening tool for rapid condition assessment in operational environments. Its ability to detect early-stage chemical changes without interrupting system operation makes it particularly attractive for preventive maintenance strategies in modern PV installations.

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