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EPOXY BARRIER COATINGS REINFORCED WITH SOLIDIFIED-WASTE MICROFILLERS FOR AGGRESSIVE ACIDS

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ABSTRACT
This paper designs and evaluates three-layer epoxy protective systems for concrete and metal substrates that incor- porate microfillers derived from solidified neutralization sludge alongside quartz flour and glass flakes to achieve high chemi- cal resistance with circular-materials benefits. Formulations are spray-applied and assessed by pull-off adhesion per EN ISO 4624, 28-day exposures to HCl, H2SO4, CH3COOH, and HNO3, and SEM of matrix–filler interfaces to confirm dispersion and interfacial cohesion. The coatings retain adhesion after HCl and H2SO4 immersion, show severe degradation in acetic acid, and exhibit marked adhesion loss in nitric acid, with failure typically in the concrete substrate except under the harshest oxidizing conditions. SEM reveals effective encapsulation of treated sludge particles within the epoxy matrix and strong interlayer bonding, indicating low risk of pollutant release during service. Critically, substituting primary fillers with solidification by-products does not diminish adhesion or chemical resistance relative to a reference epoxy system, demonstrating a viable route to sustainable polymer coatings for chemically aggressive environments.

Index Terms—Epoxy Coatings, Solidified Waste, Chemical Resistance, Microfillers, Sustainable Materials, Neutralization Sludge, Polymer Composites

I. INTRODUCTION

The increasing demand for durable construction materials in aggressive industrial environments has driven significant research into advanced protective coating systems [1]. Epoxy- based coatings have emerged as particularly suitable for such applications due to their exceptional mechanical properties, chemical resistance, and strong adhesion to various substrates [2]. However, the environmental impact of conventional coat- ing materials and the growing problem of industrial waste management have created an urgent need for more sustainable solutions that incorporate secondary raw materials without compromising performance..

Industrial activities generate substantial quantities of haz- ardous waste, including neutralization sludge from metal sur- face treatment processes, which pose significant environmental challenges [3]. Traditional disposal methods such as landfilling are increasingly viewed as unsustainable, creating pressure to develop recycling and reuse strategies for these materials [4]. The incorporation of treated hazardous waste as functional fillers in polymer coatings represents a promising approach that addresses both environmental concerns and material per- formance requirements [5].

Neutralization sludge (NS), a by-product of wastewater neutralization in metal treatment facilities, contains high levels of heavy metals such as lead and nickel, classifying it as hazardous waste according to European waste catalog code 19 02 05 [6]. Through appropriate solidification treatments using agents like fly ash and quartz flour, this waste can be transformed into stable microfillers suitable for incorporation into epoxy coating systems [7]. This approach not only reduces waste disposal requirements but also decreases the consump- tion of primary raw materials, contributing to circular economy principles in the construction industry.

The development of multi-layer coating systems allows for strategic placement of different filler types to optimize performance while ensuring environmental safety. By concen- trating waste-derived fillers in intermediate layers and using conventional or specialized fillers in surface layers, the risk of pollutant release can be effectively minimized even if the surface becomes damaged during service [8]. This layered approach represents an important innovation in the design of sustainable protective coatings for industrial applications.

This research systematically evaluates the performance of epoxy coating systems incorporating solidified neutralization sludge as microfillers, with particular focus on their adhesion to concrete substrates and resistance to various aggressive chemicals. The study also investigates the microstructural characteristics of the coatings to verify the effective encapsula- tion of waste particles within the polymer matrix. The findings demonstrate that sustainable coating solutions can achieve per- formance comparable to conventional systems while providing significant environmental benefits.

II. MATERIALS AND EXPERIMENTAL METHODS

A. Raw Materials and Preparation

The epoxy resin system used in this study was IN-EPOX 4090 (commercial name), a two-component, solvent-free for- mulation supplied by IN-CHEMIE Technology Ltd. (Olomouc, Czech Republic). This resin system exhibits excellent mechan- ical properties, chemical resistance, and UV stability, making it suitable for demanding industrial applications. The mixing ratio of component A (epoxy resin) to component B (hardener) was maintained at 2.3:1 throughout the study, with a pot life of approximately 25 minutes at 25°C and full curing achieved after 7 days under standard laboratory conditions.

The neutralization sludge (NS) used as the primary waste material was obtained from metal surface treatment operations. This hazardous waste required pretreatment before incorpora- tion into coating formulations. The sludge was initially dried at 105°C for 24 hours to remove moisture, then ground to achieve a particle size below 100 µm. The treated NS exhibited a specific gravity of 2850 kg/m³ and a specific surface area of 5400 cm²/g, with significant concentrations of lead and nickel identified through chemical analysis.

Additional materials employed in the study included fly ash (FA) from fluidized bed combustion of lignite, quartz flour (QF) with SiO content exceeding 99

B. Filler Formulation and Coating System Design

The solidification of neutralization sludge was performed using a dry homogenization method, wherein the dried NS was mixed with solidification agents (fly ash and quartz flour) in closed containers rotating at 80 rpm for 24 hours. This process ensured complete coating of NS particles with the solidification agents, effectively stabilizing the hazardous com- ponents. The homogenized mixture was subsequently milled in a laboratory vibratory disc mill and sieved through a 63 µm mesh to achieve the desired particle size distribution.

Two primary filler formulations were developed: F-NS10 containing 10

Three distinct coating systems were designed with different layer compositions, as detailed in Table I. The CS-HW10 system incorporated F-NS10 filler in the base coat, while CS- HW50 used F-NS50 filler. Both systems contained 5

TABLE I: Composition of coating system layers

Coating System	Layer	Filler	Binder
	Primer	5% NS	95% IN-ER
CS-HW10	Base coat	30% F-NS10	70% IN-ER
	Top coat	30% F-GF	70% IN-ER
	Primer	5% NS	95% IN-ER
CS-HW50	Base coat	30% F-NS50	70% IN-ER
	Top coat	30% F-GF	70% IN-ER
	Primer	5% QF	95% IN-ER
CS-REF	Base coat	30% QF	70% IN-ER
	Top coat	–	100% IN-ER

C. Testing Methods and Characterization

Adhesion testing was conducted according to EN ISO 4624 [9] using an Elcometer 506-20D pull-off adhesion tester. The coating systems were applied to concrete paving blocks (30×30 cm) with a smooth formed surface. After complete curing, metal dollies (20 mm diameter) were attached to the coating surface using a two-component epoxy adhesive. Test- ing was performed both before and after chemical exposure, with three measurements taken for each condition to ensure statistical reliability.

Chemical resistance was evaluated through 28-day exposure to four aggressive solutions: 15% HCl, 15% CHCOOH, 30% HSO, and 30% HNO. The test solutions were contained on the coating surface using sealed plastic funnels covering an areaof 80 cm ². Following exposure, the samples underwent visual assessment, adhesion testing, and microscopic examination using a Keyence VHX-950F digital microscope to evaluate degradation mechanisms and extent of damage.

Microstructural analysis was performed using a TESCAN MIRA3 XMU scanning electron microscope (SEM) to investi- gate the distribution of filler particles within the epoxy matrix, the quality of interfacial bonding, and the cohesion between different coating layers. This analysis provided critical insights into the effectiveness of waste particle encapsulation and the potential for pollutant release during service.

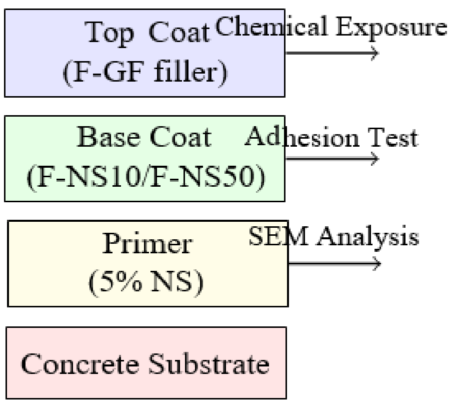

Fig. 1: Schematic of multilayer coating system and evaluation methods

III.RESULTS AND DISCUSSION

A. Adhesion Performance

The adhesion of coating systems to concrete substrates represents a critical performance parameter for protective coatings in industrial applications. Pull-off test results, graphically presented in Figure 2, demonstrated excellent initial adhesion for all coating systems, with values exceeding 2.5 MPa. This indicates strong bonding between the coating and substrate, essential for long-term durability and protection performance [10].

After 28-day exposure to 15% HCl and 30% HSO, the coating systems maintained adhesion values comparable to unexposed samples, with no statistically significant reduction observed. The failure mode in these cases occurred predominantly within the concrete substrate rather than at the coating-substrate interface, confirming the excellent bonding achieved with all formulations. This performance is particu- larly noteworthy for systems containing waste-derived fillers, demonstrating that the incorporation of solidified NS does not adversely affect adhesion properties.

In contrast, exposure to 15% CHCOOH resulted in se- vere degradation of all coating systems, rendering adhesion measurement impossible due to complete loss of integrity. The acetic acid solution penetrated through the coating layers and attacked the concrete substrate, causing extensive dam- age visible to the naked eye. For samples exposed to 30% HNO, a significant reduction in adhesion (approximately 80% compared to unexposed samples) was recorded, with failure occurring at the coating-substrate interface rather than within the concrete.

The similar performance observed for CS-HW10 and CS- HW50 systems compared to the CS-REF system indicates that the substitution of primary fillers with solidified waste mate- rials does not compromise adhesion properties. This finding has important implications for the development of sustainable coating systems, as it demonstrates that environmental bene- fits can be achieved without sacrificing critical performance characteristics.

B. Chemical Resistance Evaluation

Visual assessment and microscopic examination of coating systems after chemical exposure revealed distinct degradation patterns depending on the aggressive medium. For inorganic acids (15% HCl and 30% HSO), all coating systems exhibited excellent resistance, with only minor surface changes observed. The digital microscope images shown in Figure 3a demonstrate minimal penetration of these solutions into the coating structure, with no disruption of interlayer cohesion or adhesion to the substrate.

The superior performance against inorganic acids can be attributed to the chemical stability of the epoxy matrix and the effective barrier properties provided by the filler system. The glass flakes in the topcoat layer created a tortuous path for acid penetration, significantly slowing diffusion into the underlying layers. Furthermore, the excellent encapsulation of filler particles within the polymer matrix prevented preferential attack pathways that could compromise coating integrity.

In contrast, organic acid exposure (15% CHCOOH) caused severe degradation of all coating systems, as illustrated in Figure 3b. The acetic acid solution penetrated rapidly through the coating structure, resulting in blister formation, delamina- tion, and complete loss of protective function. This aggressive behavior of organic acids toward epoxy coatings is well- documented in the literature [11], attributed to their ability to swell the polymer matrix and disrupt cross-linking networks. Exposure to 30% HNO resulted in significant surface degradation and adhesion loss, though to a lesser extent than observed with acetic acid. As shown in Figure 3c, the nitric acid primarily attacked the epoxy matrix at the surface, with limited penetration into deeper layers. The oxidizing nature of nitric acid likely contributed to the breakdown of polymer chains, reducing cohesion within the coating matrix
and compromising adhesion to the substrate.

TABLE II: Adhesion strength (MPa) of coating systems before and after chemical exposure

Coating System	Initial	15% HCl	30% HSO	30% HNO	15% CHCOOH
CS-HW10	2.68 ± 0.21	2.59 ± 0.18	2.63 ± 0.22	0.52 ± 0.15	*
CS-HW50	2.71 ± 0.19	2.65 ± 0.23	2.60 ± 0.17	0.48 ± 0.12	*
CS-REF	2.75 ± 0.24	2.70 ± 0.20	2.68 ± 0.19	0.55 ± 0.14	-

*Measurement not possible due to complete coating degradation

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C. Microstructural Analysis

Scanning electron microscopy provided critical insights into the microstructural characteristics of the coating systems, par- ticularly regarding the distribution of waste-derived fillers and the quality of interfacial bonding. Figure 4a shows the transi- tion zone between the primer and base coat in the CS-HW50 system, demonstrating excellent cohesion between layers with no visible defects or discontinuities. This indicates that the incorporation of solidified NS fillers does not adversely affect the interlayer adhesion in multilayer coating systems.

The SEM micrograph in Figure 4b reveals the effective encapsulation of NS particles within the epoxy matrix, with strong interfacial bonding observed between the filler particles and polymer. The absence of gaps or debonding at the interface suggests effective wetting of the filler particles by the epoxy resin during mixing and application. This strong adhesion is crucial for preventing the release of hazardous substances from the waste-derived fillers during service, ensuring environmen- tal safety.

The homogeneous distribution of filler particles throughout the coating thickness, observed in multiple SEM images, contributes to the consistent performance of the coating systems. No agglomeration of NS particles was detected, indicating that the solidification and homogenization processes effectively stabilized the waste material and facilitated its dispersion within the polymer matrix. This uniform distribution likely contributes to the consistent chemical resistance and adhesion properties observed in the macroscopic testing.

The microstructural evidence supports the conclusion that properly treated neutralization sludge can be successfully incorporated into epoxy coating systems without creating defects or weak points that could compromise performance. The strong interfacial bonding and homogeneous distribution observed in the SEM analysis provide a scientific basis for the successful performance of these sustainable coating systems in aggressive environments.

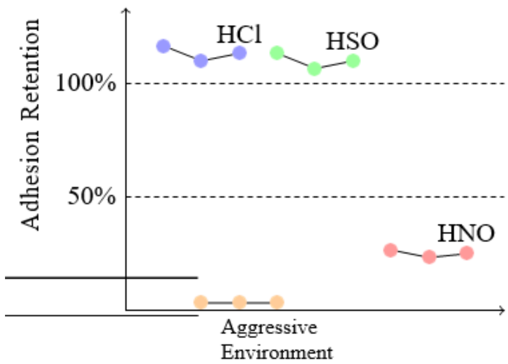

Fig. 2: Comparative adhesion retention after chemical expo- sure

IV. ENVIRONMENTAL IMPLICATIONS AND SUSTAINABILITY ASSESSMENT

The incorporation of solidified hazardous waste into pro- tective coatings represents a significant advancement in sustainable materials development for the construction industry. Traditional disposal methods for neutralization sludge, primar- ily landfilling, present ongoing environmental risks including potential leaching of heavy metals into groundwater systems [12]. The approach demonstrated in this research effectively transforms this waste stream into a valuable resource while simultaneously reducing the consumption of primary raw materials.

Life cycle assessment considerations favor the utilization of waste materials in coating systems due to reduced extraction, processing, and transportation impacts associated with conven- tional fillers. The solidification process employed in this study requires minimal energy input compared to the production of primary fillers such as quartz flour, which involves mining, crushing, grinding, and purification operations. Additionally, the avoidance of landfilling eliminates long-term monitoring and maintenance requirements for waste containment facilities.

The strategic placement of waste-derived fillers in interme- diate coating layers, rather than surface layers, provides an important safety feature that minimizes potential environmen- tal release even under conditions of partial coating damage. This design approach ensures that the hazardous components remain encapsulated within the polymer matrix throughout the service life of the coating, with multiple barriers preventing contact with the external environment.

The performance equivalence observed between coatings containing waste-derived fillers and conventional systems demonstrates that sustainability improvements need not come at the expense of technical performance. This finding challenges the common perception that environmentally friendly materials inevitably involve performance compromises, open- ing new possibilities for circular economy approaches in specialized applications such as chemical protection.

Regulatory considerations for products containing haz- ardous waste components require careful evaluation to en- sure compliance with relevant standards and regulations. The effective encapsulation demonstrated through microstructural analysis provides a scientific basis for approving such appli- cations, as the leaching potential of hazardous components is significantly reduced when properly incorporated into a stable polymer matrix. Further testing according to standardized leaching protocols would provide additional validation of this approach.

The scalability of the demonstrated technology represents an important consideration for industrial implementation. The processes for waste solidification, filler preparation, and coat- ing application employed in this research are compatible with existing industrial equipment and practices, facilitating tech- nology transfer and commercialization. The use of standard- ized testing methods and performance criteria further supports the adoption of these sustainable coating systems in practical applications.

V. PERFORMANCE MECHANISMS AND STRUCTURE-PROPERTY RELATIONSHIPS

The chemical resistance of epoxy coatings is fundamentally governed by the cross-link density of the polymer matrix, the nature of filler-matrix interactions, and the diffusion pathways available for aggressive species. The excellent performance observed against inorganic acids can be attributed to the high cross-link density of the epoxy system, which limits chain mobility and creates a tight network that resists penetration by acidic solutions. Additionally, the inert nature of the filler materials (quartz flour, fly ash, and glass flakes) ensures they do not react with acidic media, maintaining coating integrity. The platelet morphology of glass flakes in the topcoat layer creates a tortuous path for diffusing species, significantly extending the pathway that aggressive chemicals must travel to reach the substrate. This geometric barrier effect enhances the protective function of the coating, particularly against acids that primarily degrade the coating through penetration to the substrate interface. The orientation of these flakes parallel to the substrate surface, achieved through proper application techniques, maximizes this barrier effect.

The severe degradation caused by acetic acid highlights the specific vulnerability of epoxy systems to organic acids. The polar nature of acetic acid molecules enables them to interact with polar groups in the epoxy network, potentially disrupting hydrogen bonding and causing swelling of the polymer matrix. This swelling creates internal stresses that can lead to cracking, delamination, and loss of adhesion. The smaller molecular size of acetic acid compared to sulfuric or hydrochloric acid may also facilitate more rapid diffusion through the coating structure.

The strong interfacial bonding observed between waste- derived fillers and the epoxy matrix plays a crucial role in maintaining coating integrity under aggressive conditions. Weak interfaces can act as initiation points for blister for- mation and delamination, particularly in the presence of penetrating solutions that accumulate at these interfaces. The effective encapsulation of NS particles demonstrated through SEM analysis explains the maintained performance of coatings containing waste-derived fillers.

The similar performance of coatings with different NS content (10% vs. 50%) suggests that the solidification process effectively neutralizes the potential adverse effects of the waste material on coating properties. The coating of NS particles with solidification agents (fly ash and quartz flour) appears to create a stable interface that integrates well with the epoxy matrix, regardless of the waste content within the tested range. The failure mode observed in adhesion tests provides im- portant insights into the performance mechanisms. The pre- dominance of concrete substrate failure rather than interfacial failure indicates that the coating-substrate bond exceeds the cohesive strength of the concrete itself. This strong adhesion is essential for long-term protection, as it prevents underfilm corrosion and degradation that typically initiates at weak interfaces.

VI.CONCLUSIONS AND FUTURE PERSPECTIVES

This research demonstrates the successful development and evaluation of sustainable epoxy coating systems incorporating solidified neutralization sludge as microfillers. The compre- hensive testing program provides compelling evidence that properly treated hazardous waste can be effectively utilized in protective coatings without compromising performance char- acteristics. The key conclusions derived from this study are summarized below.

The adhesion of coating systems to concrete substrates remains excellent after incorporation of waste-derived fillers,exposure to inorganic acids (15% HCl and 30% HSO), the adhesion is largely maintained, with failure occurring pre- dominantly within the concrete substrate rather than at the coating interface. This demonstrates that the substitution of primary fillers with solidified waste does not adversely affect this critical performance parameter.

Chemical resistance evaluation reveals excellent perfor- mance against inorganic acids but significant vulnerability to organic and oxidizing acids. All coating systems withstand 28-day exposure to HCl and HSO with minimal degradation, while acetic acid causes complete failure and nitric acid results in substantial adhesion loss. The similar performance of coatings containing waste-derived fillers compared to the conventional reference system confirms that sustainable for- mulations can achieve equivalent protective function.

Microstructural analysis through SEM confirms effective encapsulation of waste particles within the epoxy matrix, with strong interfacial bonding and excellent cohesion between coating layers. The homogeneous distribution of filler particles and absence of defects at interfaces provide scientific evidence for the environmental safety of these coatings, as hazardous components remain effectively immobilized within the poly- mer network.

The research establishes a viable pathway for transforming hazardous waste into valuable resources for the construction industry, contributing to circular economy principles while maintaining technical performance. The processes developed for waste solidification, filler preparation, and coating ap- plication are compatible with existing industrial practices, facilitating technology transfer and implementation.

Future research should focus on expanding the range of waste materials evaluated for coating applications, optimizing solidification processes for different waste types, and devel- oping accelerated testing protocols for long-term performance prediction. Exploration of modified epoxy systems with en- hanced resistance to organic acids would address the identified vulnerability while maintaining sustainability benefits. Life cycle assessment and cost-benefit analysis would provide additional validation of the environmental and economic ad- vantages of these sustainable coating systems.

In conclusion, this research demonstrates that the integration of sustainability principles with technical performance require- ments is achievable in protective coating development. The effective utilization of hazardous waste as functional fillers represents a significant advancement in sustainable materials science, with potential applications across various sectors requiring chemical protection. The findings contribute to the growing body of knowledge supporting circular economy approaches in the construction industry.

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