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Research paper

Comparative review of alkaline and acidic etchants in chemical milling

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Abstract

Chemical milling is a widely used material removal process in aerospace, electronics, and automotive manufacturing industries. The selection of an appropriate etchant plays a crucial role in determining process efficiency, surface quality, and overall sustainability. This review examines the comparative performance of alkaline and acidic etchants based on key parameters such as etch rate, precision, material compatibility, waste management, and economic feasibility. The primary objective of this study is to analyze the strengths and limitations of both etchant types to provide insights into optimizing chemical milling processes. A structured review methodology is employed, evaluating existing literature and industrial practices to assess the influence of etchant composition on process outcomes. The analysis highlights that alkaline etchants, such as sodium hydroxide and potassium hydroxide, offer high etch rates but often result in rougher surfaces and greater undercut formation. In contrast, acidic etchants, including ferric chloride and nitric acid, provide superior surface finish, better undercut control, and enhanced precision, making them more suitable for applications requiring fine feature definition. The study also identifies key challenges in chemical milling, such as bath longevity, environmental impact, and waste disposal concerns. Future research directions include the development of eco-friendly etchants, automation-driven process optimization, and hybrid etching techniques to improve efficiency while minimizing environmental impact. The findings of this review contribute to a deeper understanding of chemical milling processes, aiding in the selection of suitable etchants for enhanced precision, cost-effectiveness, and sustainability.

Keywords: *Acidic Etchants; Alkaline Etchants; Chemical Milling; Etchants; Etching Solution.*

1. Introduction

Chemical milling is a widely employed material removal technique in aerospace, automotive, and electronics industries, where precision and surface integrity are critical. This process involves controlled chemical etching to achieve desired component geometries while minimizing mechanical stress [1], [2]. However, the selection of a suitable etchant significantly impacts process efficiency, etch rate, dimensional accuracy, surface roughness, and environmental sustainability [3], [4].

The primary challenge lies in understanding the trade-offs between alkaline and acidic etchants concerning their chemical reactivity, process stability, and long-term feasibility. Existing research predominantly focuses on individual etchants or specific materials, with limited comparative studies that systematically analyze their performance across various process parameters. Figure 1 presents the various chemical milling process parameters.

To address this gap, this review provides a comprehensive evaluation of alkaline and acidic etchants, identifying their advantages, limitations, and industrial relevance. The study examines key performance factors, including etch rate, precision, undercut formation, surface finish, material compatibility, process stability, environmental impact, and economic considerations. By synthesizing available literature and experimental insights, this review aims to establish a structured understanding of chemical milling mechanisms and their implications for manufacturing efficiency.

The findings are expected to provide valuable insights into optimizing chemical milling operations, guiding industry professionals in selecting appropriate etchants, and promoting sustainable etching technologies. Additionally, this review underscores the need for future research into eco-friendly etchants, automation-driven process control, and hybrid etching techniques to enhance precision and reduce environmental impact.

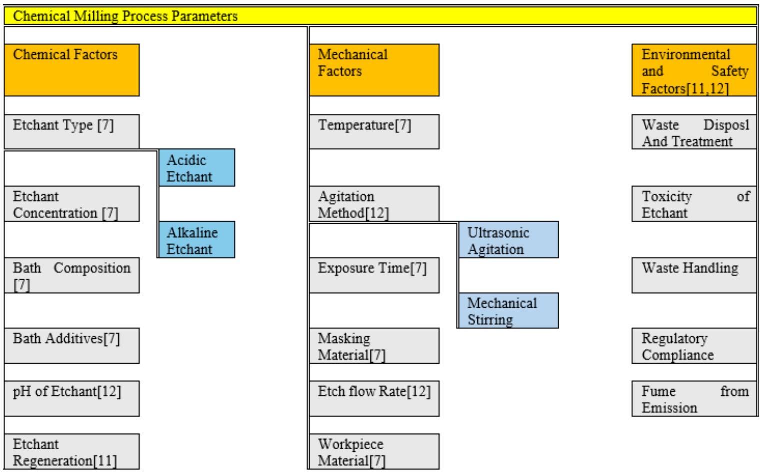

Fig. 1: Chemical Milling Process Parameters.

2. Background of study and related work

2.1. Background of the study

Chemical milling is an essential material removal process widely utilized in industries such as aerospace, automotive, and electronics due to its ability to produce intricate geometries without inducing mechanical stress. The technique relies on selective chemical dissolution using either acidic or alkaline etchants to achieve precise material removal while maintaining structural integrity [1], [2]. Over the years, researchers have explored various etchant compositions, process parameters, and waste management strategies to optimize chemical milling for different materials. However, despite advancements, challenges related to process stability, etch rate control, surface quality, environmental impact, and economic feasibility persist [1], [5], [6]. Figure 2 shows undercutting, where lateral etching extends beneath the protective mask, thereby compromising dimensional accuracy.

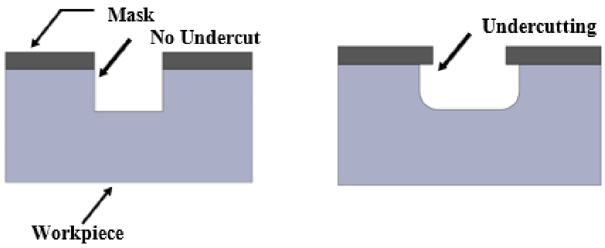

Fig. 2: Undercutting in Chemical Milling.

Acidic etchants, such as ferric chloride and nitric acid, are commonly used due to their high etching efficiency and material compatibility. However, they present challenges related to hazardous byproducts, corrosion control, and waste disposal [5], [8]. Alkaline etchants, such as sodium hydroxide and potassium hydroxide, offer alternative solutions, particularly for aluminum and other reactive metals. While these etchants generate less hazardous waste, they often suffer from issues such as sludge formation, non-uniform etching, and process inconsistency [9]. The increasing demand for sustainable and high-precision etching has led to research on eco-friendly etchants, hybrid etching techniques, and automation-based process monitoring. Innovations such as deep eutectic solvents (DES), ionic liquids, and laser-assisted etching have demonstrated potential in enhancing process efficiency while minimizing environmental impact [10]. However, a comprehensive comparative analysis of existing etching techniques is still lacking, necessitating a structured evaluation of both alkaline and acidic etchants concerning their process performance and sustainability.

2.2. Related work

Numerous studies have investigated the application of chemical milling for different materials and industrial applications. Researchers have focused on optimizing etching parameters such as temperature, etchant concentration, and agitation to improve precision and minimize surface defects [7], [9-14]. Advancements in chemical milling have also explored automation and real-time monitoring systems to enhance process reliability. AI-driven predictive models and sensor-based etchant monitoring have been proposed to improve process stability and reduce material wastage [15]. While non-chemical milling techniques like laser ablation, plasma etching, and mechanical micromachining are widely used in advanced manufacturing, chemical milling retains several key advantages. First, chemical etching offers uniform material removal over large areas without requiring complex motion control or thermal management. This makes it ideal for producing thin metal components such as foils, meshes, and aerospace shims. Moreover, chemical milling is a cost-effective and scalable technique for batch production of parts with high dimensional accuracy, particularly when intricate geometries are required. Recent advancements in additive manufacturing (AM) have highlighted the need for effective post-processing methods to achieve high surface finish and dimensional precision. Chemical milling offers a viable solution for refining AM components, particularly in removing surface roughness and fine-tuning geometries without inducing mechanical stress. Exploring the integration of chemical milling in AM workflows could open new pathways for hybrid manufacturing approaches that combine design flexibility with surface engineering precision [16]. Additionally, hybrid approaches integrating electrochemical etching, plasma-assisted etching, and chemical-mechanical polishing have shown promise in achieving superior surface quality and precision [10], [15]. However, these techniques often involve high capital costs and complex control systems, limiting their widespread industrial adoption compared to chemical milling. Recent research also explores bio-based etchants derived from plant extracts and nanoparticle-enhanced solutions, which offer improved selectivity and reduced environmental toxicity. These alternatives, although in early stages, present potential for sustainable etching with controlled reaction kinetics [17-19]. This section presents a detailed discussion of existing studies on acidic and alkaline etchants, their influence on etching performance, and efforts to improve process efficiency and sustainability.

2.2.1. Studies on acidic etchants

Table 1 presents commonly used acidic etchants and their performance for key parameters from the literature. Studies on ferric chloride-based etching have highlighted its effectiveness for stainless steel and copper [12], [13], but concerns regarding waste treatment and metal ion accumulation remain unresolved. The preference for certain etchants in specific applications is primarily driven by a combination of material compatibility, process efficiency, and economic factors. For example, ferric chloride ($FeCl_3$) is the dominant etchant for stainless steel due to its ability to effectively dissolve iron oxides, leading to uniform material removal with minimal surface roughness [4]. Acidic etchants, particularly ferric chloride, nitric acid, and hydrofluoric acid, are commonly used due to their high etch rates and material compatibility [1], [2], [24], [21]. Research by various authors has demonstrated that ferric chloride provides rapid metal dissolution but requires precise control over oxidation states to maintain etching consistency [7], [22]. Studies indicate that ferric chloride works effectively on copper, stainless steel, and titanium but leads to excessive undercut and surface roughness issues[23]. Nitric acid, widely used for aluminum etching, has been analyzed for its role in passivation layer removal, but concerns related to nitrate-based waste disposal remain unresolved [1], [4], [24].

Table 1: Commonly Used Acidic Etchants and Their Performance [4], [5]

Etchants	Materials	Concentration	Etching Temp (°C)	Etch Rate (mm/min)
FeCl3	Aluminium and alloys	12-18^0 Bé (*)	49	0.013-0.025
	Copper and alloys	42^0 Bé	49	2
	Steel	42^0 Bé	54	0.025
	Nickel	42^0 Bé	49	0.13-0.38
HF	Titanium	--	--	1
	Glass	--	--	--
HNO3	Magnesium	%12-15	32-49	1
	Silicon	--	38-49	Very slow

(The Baumé scale, Baumé degrees (°Bé), is a hydrometer scale used to measure the density of liquids; in etchant formulation, it indicates solution concentration. Baumé [Bé] value is Bé = 145 × [(sg – 1)/sg], where sg = specific gravity).

Hydrofluoric acid (HF) has been extensively examined for its effectiveness in magnesium and titanium etching, particularly in aerospace component manufacturing [1], [4], [6]. However, its high toxicity and aggressive reaction rates pose challenges in handling, waste management, and regulatory compliance [20]. Research has been conducted to explore alternative etchants or buffered HF solutions to improve etch selectivity and process stability [20], [25]. Some studies have also investigated the impact of etchant concentration, temperature, and agitation on etching uniformity and defect minimization in acidic etching processes.

2.2.2. Studies on alkaline etchants

Table 2 presents commonly used acidic etchants and their performance concerning key parameters from the literature. Alkaline etchants, primarily based on sodium hydroxide (NaOH) and potassium hydroxide (KOH), have been studied as alternatives to acidic solutions due to their better selectivity and environmentally friendly characteristics. Sodium hydroxide (NaOH) is predominantly used for aluminum because of its rapid dissolution of aluminum oxides and the formation of soluble sodium aluminate. These preferences are not only based on chemical reactivity but also on factors such as cost efficiency, ease of handling, and environmental impact. Research has shown that alkaline etchants are effective in etching aluminum, silicon, and certain magnesium alloys, producing cleaner etch profiles with lower undercut formation [26].

Table 2: Commonly Used Alkaline Etchants and Their Performance [10]

Etchants	Materials	Concentration	Etching Temp (°C)	Etch Rate (mm/min)
NaOH	Aluminium	1 mol	30	0.0013
			50	0.004
KOH	Aluminium	1 mol	30	0.001
			50	0.0025

However, their low etch rates and precipitation of metal hydroxides create challenges in maintaining etching efficiency over extended process cycles [8]. Several studies have examined the role of additives, inhibitors, and complexing agents in alkaline etching solutions to enhance etch uniformity and reduce sludge formation. The addition of chelating agents such as EDTA and gluconates has been explored to prolong bath life and stabilize dissolved metal ions [8], [27-30]. Moreover, alkaline etching has been integrated with electrochemical processes to improve etch precision and material removal control [19], [31]. Despite these advantages, the scalability of alkaline etchants remains an issue due to difficulties in bath regeneration and waste treatment.

2.2.3. Hybrid etching techniques

Unlike conventional wet or dry methods, which often face challenges related to anisotropy, surface quality, or material compatibility, hybrid methods integrate complementary processes to achieve improved outcomes. To overcome the limitations of conventional acidic and alkaline etching, researchers have proposed hybrid etching techniques combining chemical milling with laser-assisted etching, plasma etching, and electrochemical machining (ECM). Studies indicate that hybrid approaches can enhance etch precision, reduce chemical consumption, and minimize environmental impact. Laser-assisted etching, for instance, selectively modifies surface regions to improve etch selectivity, while ECM integrates electrical field-assisted etching to control material removal rates [9], [19], [31-33]. Recent studies have also focused on using DES and ionic liquids as green etchants, aiming to replace hazardous chemicals like ferric chloride and hydrofluoric acid [34-36]. Preliminary research suggests that these novel etchants exhibit high selectivity and recyclability, making them promising candidates for sustainable chemical milling processes. However, further investigations are required to assess their industrial feasibility, cost-effectiveness, and compatibility with existing manufacturing systems.

2.2.4. Automation and process optimization

One of the major challenges in chemical milling is the lack of real-time process control compared to conventional CNC machining techniques. Several studies have explored the potential of AI-driven process monitoring, predictive modeling, and real-time bath analysis to enhance etching precision and reproducibility [13], [14], [37], [38]. Automated chemical handling systems, equipped with sensors for pH, temperature, and metal ion concentration, have been developed to improve process stability and efficiency.

Some research efforts have also focused on closed-loop etchant regeneration systems, incorporating electrochemical metal recovery and membrane filtration technologies to extend bath life and reduce waste generation [39-41]. While these advancements show promise, their industrial adoption remains limited due to cost constraints and integration challenges with existing production lines. Additionally, researchers have evaluated life cycle assessments (LCA) to compare the environmental footprint of different etching techniques, emphasizing the need for sustainable alternatives. Future studies are expected to explore integrated waste recovery systems that allow for continuous metal extraction and etchant reuse, thereby reducing costs and enhancing sustainability.

2.2.5. Environmental and waste management studies

The environmental impact of chemical milling has been a key area of study, particularly concerning waste etchant disposal, heavy metal contamination, and sludge management. Various researchers have examined neutralization, ion-exchange purification, and zero-liquid discharge (ZLD) technologies to mitigate chemical waste disposal issues [42-44]. Studies on bio-based neutralizing agents and green precipitation methods have demonstrated potential in reducing hazardous byproducts, yet scalability and economic feasibility remain concerns for industrial applications [45].

2.2.6. Research gaps and future Scope

Although significant progress has been made in chemical milling research, several gaps remain, such as limited studies on specific etchant-metal interactions, particularly for advanced alloys and composite materials, and a lack of standardized process parameters, making cross-comparisons between different studies challenging. There is insufficient research on hybrid etching techniques and their industrial-scale implementation. The need for automation and AI-based process optimization to enhance precision and consistency remains unexplored. Aspects such as environmental concerns related to waste disposal and sustainability, and eco-friendly etching alternatives require further investigation.

Future research should focus on developing standardized testing methodologies, improving process automation, and advancing sustainable chemical milling technologies to enhance industrial efficiency and environmental responsibility.

3. Research method

This review paper employs a systematic literature review (SLR) approach to analyze and compare the performance of alkaline and acidic etchants in chemical milling. The methodology involves three key stages: literature collection, data extraction, and comparative analysis, ensuring a comprehensive evaluation of existing research on chemical milling processes, their challenges, and future advancements.

3.1. Literature collection

A structured literature search was conducted using peer-reviewed journals, conference proceedings, and industrial reports from recognized scientific databases such as Scopus, Web of Science, and Google Scholar. The selection criteria focused on studies that investigated etch rate, surface roughness, undercut formation, waste management, and economic feasibility of chemical milling using acidic and alkaline etchants. Only articles published in the last two decades were prioritized to ensure the inclusion of recent advancements and industrial developments.

3.2. Data extraction and categorization

The collected literature was systematically analyzed to extract relevant data on process parameters, material compatibility, and sustainability aspects. The extracted data were categorized based on the following key performance indicators [1], [2], [4] namely etch rate: speed of material removal under different etching conditions, surface roughness: impact of etching on the final surface finish, undercut formation: degree of lateral etching affecting dimensional precision, waste generation and environmental impact: volume and toxicity of byproducts and economic feasibility: cost-effectiveness of etchants in industrial applications. A comparative mapping approach was used to systematically evaluate the influence of etchant type (acidic vs. alkaline) on these parameters for different materials such as aluminum, stainless steel, copper, titanium, and magnesium.

3.3. Comparative analysis and evaluation

A qualitative and quantitative comparison of alkaline and acidic etchants was conducted based on the extracted data. Studies that reported experimental findings on etch rate, undercut, and surface integrity were carefully analyzed to establish trends and correlations between etchant composition and material performance. Additionally, waste treatment strategies and environmental implications were assessed to determine the sustainability of different etching approaches. The results were synthesized to identify research gaps, emerging trends, and potential future directions for improving chemical milling processes. This structured approach ensures a holistic evaluation of chemical milling techniques, providing insights into optimizing etching performance while addressing sustainability challenges.

4. Results and discussion

This section presents a comparative evaluation of alkaline and acidic etchants in chemical milling, focusing on key performance indicators such as etch rate, surface roughness, undercut formation, waste management, and economic feasibility. Moreover, process parameters critically influence etching outcomes. For instance, elevated temperatures accelerate reaction kinetics but may compromise dimensional control. Similarly, higher agitation levels improve mass transport yet risk over-etching. These interactions highlight the importance of optimizing etching protocols for targeted applications, particularly when balancing precision and throughput [1],[2],[4]. The extracted data from various studies have been systematically analyzed to identify trends, challenges, and potential improvements in the chemical milling process.

4.1. Comparative analysis of etch performance

The results indicate that acidic etchants generally exhibit higher etch rates, making them suitable for applications requiring faster material removal. However, they often result in higher undercut formation, impacting precision. In contrast, alkaline etchants offer better selectivity and controlled material removal, reducing undercut, but at the cost of slower etch rates. Alkaline etchants, although highly effective for bulk etching, often exhibit non-uniform depth profiles, particularly if process conditions such as temperature and etchant concentration are not carefully regulated. Surface uniformity is another critical factor in evaluating etchant performance [1]. Acidic etchants are known for their superior uniformity, as they dissolve the metal surface more evenly, reducing the likelihood of rough textures or excessive pitting. This makes them preferable for applications requiring high surface integrity, such as printed circuit boards (PCBs) and medical implants. Alkaline etchants often produce rougher surfaces and require additional post-processing to achieve the desired finish.

4.1.1. Etch rate and material compatibility

Aluminum and copper show higher etch rates in acidic solutions like ferric chloride and nitric acid due to their strong oxidizing properties [10], [12]. Stainless steel and titanium require specialized etchant compositions to achieve efficient material removal while maintaining structural integrity [20]. Alkaline etchants, such as sodium hydroxide and potassium hydroxide, demonstrate controlled etching, especially for materials like silicon and magnesium, which are highly reactive to acids [26], [47], [48].

4.2. Surface roughness and dimensional accuracy

Surface roughness is a critical parameter in determining the quality of chemically milled components. Studies indicate that Acidic etchants often lead to an increase in surface roughness due to aggressive dissolution and localized variations in reaction rates. While alkaline etchants are known for offering controlled etching and selectivity, they may still contribute to surface roughness under certain conditions due to gas bubble formation and sludge accumulation. Therefore, their effectiveness in minimizing surface defects is context-dependent and influenced by parameters such as agitation, temperature, and concentration control. Alkaline etchants, particularly those containing inhibitors, help achieve smoother surfaces by slowing down reaction kinetics [49]. Gas bubble formation in alkaline etching can cause localized defects, requiring agitation techniques to ensure uniform material removal [2].

4.3. Undercut formation and process control

Undercutting occurs due to lateral etching, which can compromise the precision of chemically milled components. The analysis reveals that acidic etchants contribute to significant undercut formation, necessitating the use of inhibitors to reduce lateral material removal. Alkaline etchants, though offering better control, require precise process parameters such as temperature and agitation control to maintain consistency [49]. The integration of automated monitoring systems could improve process control, enabling real-time adjustments to optimize etching performance.

4.4. Waste management and environmental impact

One of the major drawbacks of chemical milling is the generation of toxic waste, including metal-laden etchant solutions and sludge. Key findings suggest alkaline etchants produce metal hydroxide sludge, requiring frequent filtration and disposal [8]. Acidic etchants generate metal-rich wastewater, necessitating advanced treatment methods such as precipitation, ion exchange, and electrochemical recovery [7]. The use of closed-loop regeneration systems for ferric chloride and nitric acid etchants has shown promise in reducing chemical consumption and waste generation. These environmental challenges underscore the urgent need for sustainable innovations discussed in the subsequent section. Future etching technologies must not only improve material performance but also align with stricter environmental regulations and circular economy principles.

4.5. Economic feasibility and industrial implementation

The cost-effectiveness of chemical milling is influenced by etchant longevity, waste disposal costs, and operational efficiency. Findings from the reviewed literature suggest that acidic etchants, while more efficient, require frequent regeneration and stricter waste treatment measures, increasing operational costs [7]. Alkaline etchants offer better recyclability, but their tendency to form sludge leads to higher maintenance costs [8]. The adoption of eco-friendly etchants, such as DES and ionic liquids, could significantly reduce environmental and economic burdens. While the shift toward environmentally benign etchants such as deep eutectic solvents, bio-based acids, and ionic liquids is crucial for sustainable manufacturing, these solutions often incur higher initial material costs and require new process validation. A preliminary cost-benefit analysis suggests that although these green technologies may increase short-term operational expenses, they can yield long-term savings by reducing hazardous waste treatment, minimizing regulatory compliance costs, and improving worker safety [46].

4.6. Future prospects, challenges, and technological advancements

Despite the extensive analysis, this review has certain limitations. The lack of standardized testing methodologies across studies limits direct comparisons, while the focus on specific etchant-material interactions leaves many industrially relevant materials underexplored. Additionally, the effects of key process parameters such as temperature, agitation, and inhibitor concentration require further systematic investigation to establish precise correlations with etching performance. The industrial-scale feasibility of hybrid etching techniques remains largely unexamined, requiring experimental validation to apply laboratory findings to large-scale applications.

Future research should prioritize standardized experimental studies to enable cross-comparability of etchant performance. The exploration of novel eco-friendly etchants, such as DES and ionic liquids, presents a promising alternative to conventional hazardous chemicals. Integrating automation technologies, including AI-driven process control and real-time etchant monitoring, can significantly enhance precision and reproducibility. Furthermore, hybrid etching methods combining chemical milling with laser-assisted, plasma, or electrochemical machining warrant investigation to optimize process efficiency. Future research should explore the integration of environmentally friendly etchants in additive manufacturing, especially for post-processing metal-printed components. This could enhance compatibility between subtractive and additive technologies while reducing overall environmental impact. Additionally, a life cycle assessment of etchants could provide insights into their contribution to carbon footprint reduction across various industrial sectors.

Addressing these gaps will drive advancements in chemical milling, making it more efficient, cost-effective, and environmentally sustainable. To address the challenges in chemical milling, emerging research is exploring hybrid etching techniques, such as combining chemical milling with laser-assisted etching and electrochemical machining, to enhance precision and reduce chemical consumption. Research is also being conducted into AI-driven process optimization for real-time control of etching parameters, improving reproducibility in industrial applications. Green chemistry approaches, including biodegradable etchants, to minimize environmental impact while maintaining high etch selectivity, is another emerging area. The growing use of hybrid materials necessitates a deeper understanding of how chemical etchants interact with heterogeneous phases. As composites become increasingly prevalent in aerospace and electronics, their layered structures and mixed-phase constituents pose unique challenges in etchant penetration, selectivity, and surface degradation.

4.7. Summary of findings

The comparative analysis highlights that while acidic etchants provide higher etch rates, they present challenges in precision, waste management, and economic feasibility. Alkaline etchants offer better process control and lower environmental impact, but their effectiveness varies depending on the material. The development of eco-friendly etching solutions and automation-driven process improvements presents a promising direction for advancing chemical milling technology. Similarly, while hybrid techniques such as laser-assisted etching and electrochemical machining show promise in laboratory-scale trials, their full-scale industrial adoption remains limited due to high initial costs, integration complexity, and the need for specialized infrastructure. Table 3 presents the mapping of performance parameters for different materials processed by chemical milling with alkaline and acidic etchants.

Table 3: Mapping of Referenced Literature with Performance Parameters for Different Materials with Alkaline and Acidic Etchants

	Acidic			Alkaline		
Material	Surface Roughness	Undercut	Etch Rate	Surface Roughness	Undercut	Etch Rate
Stainless Steel	[11], [21]	@	[4], [21]	[53]	@	@
Aluminium	[5], [10]	@	[4], [10]	[10]	@	[10]
Copper	[12]	[49]	[4], [12]	@	[29], [30]	[29], [30]
Magnesium	[50]	[50]	[50]	@	@	@
Nickel	@	@	[4]	@	@	@
Titanium	[20], [51], [52]	@	[20], [51], [52]	[54]	@	@
Silicon	@	@	@	[26]	[26]	[26]

@ Future scope.

5. Conclusion

This review presents a comprehensive evaluation of alkaline and acidic etchants in chemical milling, analyzing their impact on etch rate, precision, surface roughness, material compatibility, waste management, and economic feasibility. The findings indicate that acidic etchants generally achieve higher etch rates but lead to increased undercut and waste generation, posing challenges for precision applications. While alkaline etchants often exhibit improved selectivity, especially for aluminum-based substrates, this is not a universal outcome. Selectivity is influenced by factors such as alloy composition, etchant formulation, and agitation level. Similarly, emerging green alternatives like deep eutectic solvents and ionic liquids offer potential for sustainable chemical milling; however, their industrial adoption is still limited by cost, handling complexity, and lack of large-scale performance data. Future research should focus on validating the performance of Deep Eutectic Solvents (DES) and other emerging green etchants in real-world industrial settings. This includes testing their effectiveness in large-scale chemical milling processes and assessing their compatibility with different materials. This study advances the existing body of knowledge by categorizing etchants based on key performance parameters, highlighting the environmental and economic challenges associated with conventional etching methods, and identifying critical research gaps related to etchant composition, process automation, and sustainable alternatives. The review underscores the potential of hybrid etching techniques and automation-driven process control in enhancing precision and sustainability in chemical milling. This review also highlights the broader implications for regulatory compliance, particularly regarding the European REACH regulations, which increasingly mandate the use of eco-friendly and non-toxic chemicals in industrial processes. By selecting sustainable etchants and optimizing milling techniques, manufacturers couldn't ensure compliance with stringent environmental regulations. Furthermore, adopting regeneration technologies can extend etchant longevity, lowering waste disposal costs. The transition toward eco-friendly etching solutions can also help industries navigate regulatory compliance challenges while reducing the environmental footprint of chemical milling.

References

[1] El-Hofy, H. (2005). *Advanced machining processes: Nontraditional and hybrid machining processes*. McGraw-Hill.

[2] Bhattacharyya, B., & Doloi, B. (2020). Machining processes utilizing chemical and electrochemical energy. In *Modern Machining Technology* (pp. 365–460). Elsevier. https://doi.org/10.1016/B978-0-12-812894-7.00005-0.

[3] Ikumapayi, O. M., et al. (2023). Non-traditional machining techniques in manufacturing industries – An overview. *E3S Web of Conferences, 430*, 01213. https://doi.org/10.1051/e3sconf/202343001213.

[4] Cakir, O., Yardimeden, A., & Ozben, T. (2007). Chemical machining. *Archives of Materials Science and Engineering, 28*.

[5] Rohith, R., et al. (2022). Chemical machining process – A review. *Proceedings on Engineering Sciences, 4*(1), 33–36. https://doi.org/10.24874/PES04.01.005.

[6] Kumar, A., Apoorva, S., Ashwin Kumar, S. B., Sumanth, H. U., & Nanjundeswaraswamy, T. S. (2019). Chemical blanking and chemical milling process: An outline. *International Journal of Engineering Research and Applications (IJERA), 9*(10), 83–86.

[7] Yu, M., et al. (2016). Examining regeneration technologies for etching solutions: A critical analysis of the characteristics and potentials. *Journal of Cleaner Production, 113*, 973–980. https://doi.org/10.1016/j.jclepro.2015.10.131.

[8] Kape, J. M. (1970). Chemical etching of aluminium in caustic soda based solutions. *Transactions of the IMF, 48*(1), 43–50. https://doi.org/10.1080/00202967.1970.11870128.

[9] Wang, J., et al. (2022). Research status and prospect of laser scribing process and equipment for chemical milling parts in aviation and aerospace. *Micromachines, 13*(2), 323. https://doi.org/10.3390/mi13020323.

[10] Çakır, O. (2019). Etchants for chemical machining of aluminium and its alloys. *Acta Physica Polonica A, 135*(4), 586–587. https://doi.org/10.12693/APhysPolA.135.586.

[11] Çakır, O. (2007). Study of etch rate and surface roughness in chemical etching of stainless steel. *Key Engineering Materials, 364–366*, 837–842. https://doi.org/10.4028/www.scientific.net/KEM.364-366.837.

[12] Çakır, O. (2007). Review of etchants for copper and its alloys in wet etching processes. *Key Engineering Materials, 364–366*, 460–465. https://doi.org/10.4028/www.scientific.net/KEM.364-366.460.

[13] Patil, O., & Chanmanwar, R. (2018). Analysis and optimization of photochemical machining on copper. *Procedia Computer Science, 133*, 464–470. https://doi.org/10.1016/j.procs.2018.07.057.

[14] Saraf, A. R., & Sadaiah, M. (2013). Application of artificial intelligence for the prediction of undercut in photochemical machining. *International Journal of Machining and Machinability of Materials, 6*(2), 183. https://doi.org/10.1504/IJMMS.2013.053829.

[15] Saraf, A. R., & Sadaiah, M. (2017). Magnetic field-assisted photochemical machining (MFAPCM) of SS316L. *Materials and Manufacturing Processes, 32*(3), 327–332. https://doi.org/10.1080/10426914.2016.1198014.

[16] Mathew, A., Kishore, S. R., Tomy, A. T., Sugavaneswaran, M., Scholz, S. G., Elkaseer, A., Wilson, V. H., & John Rajan, A. (2023). Vapour polishing of fused deposition modelling (Fdm) parts: A critical review of different techniques, and subsequent surface finish and mechanical properties of the post-processed 3D-printed parts. Progress in Additive Manufacturing, 8(6), 1161–1178. https://doi.org/10.1007/s40964-022-00391-7.

[17] Broekaert, T. P. E., & Fonstad, C. G. (1992). Novel, organic acid-based etchants for ingaalas / inp heterostructure devices with alas etch-stop layers. Journal of The Electrochemical Society, 139(8), 2306–2309. https://doi.org/10.1149/1.2221220.

[18] DeSalvo, G. C., Tseng, W. F., & Comas, J. (1992). Etch rates and selectivities of citric acid/hydrogen peroxide on GaAs , $Al_{0.3}Ga_{0.7}As$, $In_{0.2}Ga_{0.8}As$, $In_{0.53}Ga_{0.47}As$, $In_{0.52}Al_{0.48}As$, and InP. Journal of The Electrochemical Society, 139(3), 831–835. https://doi.org/10.1149/1.2069311.

[19] Jung, K., & Lee, J. (2024). A review of the mechanism and optimization of metal-assisted chemical etching and applications in semiconductors. Micro and Nano Systems Letters, 12(1), 27. https://doi.org/10.1186/s40486-024-00217-x.

[20] Xu, H., et al. (2006). Chemical etching solutions for titanium and titanium alloys. *CN1743508A*. Retrieved from https://patents.google.com/patent/CN1743508A/en

[21] Prasad, A. R., & Prakash, S. (2023). A review on anodizing process of aluminum and non-aluminium alloys. *[Unpublished manuscript]*.

[22] Beyer, S., & Lukes, R. (1974). Regeneration of ferric chloride copper etching solutions. *US Patent 3794571A*. https://worldwide.espacenet.com/patent/search/family/022498424/publication/US3794571A.

[23] Patil, D. H., Thorat, S. B., Khake, R. A., & Mudigonda, S. (2018). Comparative study of $FeCl_3$ and $CuCl_2$ on geometrical features using photochemical machining of Monel 400. *Procedia CIRP, 68*, 144–149. https://doi.org/10.1016/j.procir.2017.12.084.

[24] Choi, K., Kim, S., Lee, J., Chu, B., & Jeong, D. (2024). Eco-friendly glass wet etching for MEMS application: A review. *Journal of the American Ceramic Society, 107* (10), 6497–6515. https://doi.org/10.1111/jace.19961.

[25] Dumbre, J., Tong, Z., Dong, D., Qiu, D., & Easton, M. (2024). Buffered oxide etch: A safer, more effective etchant for additively manufactured Ti-alloys. *Metallography, Microstructure, and Analysis, 13*(5), 871–879. https://doi.org/10.1007/s13632-024-01094-x.

[26] Zubel, I., Barycka, I., Kotowska, K., & Kramkowska, M. (2001). Silicon anisotropic etching in alkaline solutions IV. *Sensors and Actuators A: Physical, 87*(3), 163–171. https://doi.org/10.1016/S0924-4247(00)00481-7.

[27] Solvay Solutions UK Ltd. (1981). *Etching composition*. GB Patent No. GB2067958A. https://worldwide.espacenet.com/patent/search/family/026274270/publication/GB2067958A.

[28] Sesana, R., Spriano, S., Ferraris, S., & Matteis, P. (2019). Fatigue resistance of light alloy sheets undergoing eco-friendly chemical milling: Metallurgical and chemical aspects. *Procedia Structural Integrity, 19*, 362–369. https://doi.org/10.1016/j.prostr.2019.12.039.

[29] Murski, K. J. (1982). *Ammoniacal alkaline cupric etchant solution for and method of reducing etchant undercut* (US Patent No. 4319955A). https://worldwide.espacenet.com/patent/search/family/022757083/publication/US4319955A.

[30] Chiang, J. (1974). *Process of etching copper circuits with alkaline persulfate and compositions therefore* (US Patent No. 3837945A). https://worldwide.espacenet.com/patent/search/family/022891621/publication/US3837945A.

[31] Taylor, E., & Sun, J. (2005). *Electrochemical etching of circuitry for high density interconnect electronic modules* (US Patent No. US20050145506A1). https://worldwide.espacenet.com/patent/search/family/034710805/publication/US2005145506A1.

[32] Stephen, A. (2011). Mechanisms and applications of laser chemical machining. *Physics Procedia, 12*, 261–267. https://doi.org/10.1016/j.phpro.2011.03.132.

[33] Leone, C., Lopresto, V., Memola Capece Minutolo, F., De Iorio, I., & Rinaldi, N. (2010). Laser ablation of maskant used in chemical milling process for aerospace applications. In T. Dreischuh, P. A. Atanasov, & N. V. Sabotinov (Eds.), *Proceedings of SPIE*, 77511M–77511M–9. https://doi.org/10.1117/12.876386.

[34] Smith, E. L., Abbott, A. P., & Ryder, K. S. (2014). Deep eutectic solvents (DESs) and their applications. *Chemical Reviews, 114*(21), 11060–11082. https://doi.org/10.1021/cr300162p.

[35] Lomba, L., García, C. B., Ribate, M. P., Giner, B., & Zuriaga, E. (2021). Applications of deep eutectic solvents related to health, synthesis, and extraction of natural based chemicals. *Applied Sciences, 11*(21), 10156. https://doi.org/10.3390/app112110156.

[36] Kityk, A., Pavlik, V., & Hnatko, M. (2023). Exploring deep eutectic solvents for the electrochemical and chemical synthesis of photo- and electrocatalysts for hydrogen evolution. *International Journal of Hydrogen Energy, 48*(100), 39823–39853. https://doi.org/10.1016/j.ijhydene.2023.07.158.

[37] Nelson, C. (1985). *Method and apparatus for automated chemical milling of compound curved surfaces* (US Patent No. 4523973A). https://worldwide.espacenet.com/patent/search/family/024165286/publication/US4523973A.

[38] Jaffe, H. R., & Mitzelman, I. (1986). *Automated chemical milling process* (US Patent No. 4585519A). https://worldwide.espacenet.com/patent/search/family/023848135/publication/US4585519A.

[39] Chang, Y., et al. (2018). Closed-loop electrochemical recycling of spent copper (II) from etchant wastewater using a carbon nanotube modified graphite felt anode. *Environmental Science & Technology, 52*(10), 5940–5948. https://doi.org/10.1021/acs.est.7b06298.

[40] Sun, Z., Xiao, Y., Sietsma, J., Agterhuis, H., & Yang, Y. (2015). A cleaner process for selective recovery of valuable metals from electronic waste of complex mixtures of end-of-life electronic products. *Environmental Science & Technology, 49*(13), 7981–7988. https://doi.org/10.1021/acs.est.5b01023.

[41] Rai, V., Liu, D., Xia, D., Jayaraman, Y., & Gabriel, J.-C. P. (2021). Electrochemical approaches for the recovery of metals from electronic waste: A critical review. *Recycling, 6*(3), 53. https://doi.org/10.3390/recycling6030053.

[42] Lee, J., Shin, Y., Ryu, H., Boo, C., & Hong, S. (2025). Toward zero liquid discharge treatment of semiconductor wastewaters with a hybrid system integrating forward osmosis and multi-stage nanofiltration. *Water Research, 279*, 123410. https://doi.org/10.1016/j.watres.2025.123410.

[43] Aoudj, S., Khelifa, A., & Drouiche, N. (2017). Removal of fluoride, SDS, ammonia and turbidity from semiconductor wastewater by combined electrocoagulation–electroflotation. *Chemosphere, 180*, 379–387. https://doi.org/10.1016/j.chemosphere.2017.04.045.

[44] Chatla, A., et al. (2023). Sulphate removal from aqueous solutions: State-of-the-art technologies and future research trends. *Desalination, 558*, 116615. https://doi.org/10.1016/j.desal.2023.116615.

[45] Pines Pozo, M. T., Lopez Fernandez, E., Villaseñor, J., Leon-Fernandez, L. F., & Fernandez-Morales, F. J. (2025). Metal recovery from wastes: A review of recent advances in the use of bioelectrochemical systems. *Applied Sciences, 15*(3), 1456. https://doi.org/10.3390/app15031456.

[46] Nahar, Y., & Thickett, S. C. (2021). Greener, faster, stronger: The benefits of deep eutectic solvents in polymer and materials science. Polymers, 13(3), 447. https://doi.org/10.3390/polym13030447.

[47] Shah, I. A., Koekkoek, A. J. J., Van Enckevort, W. J. P., & Vlieg, E. (2009). Influence of additives on alkaline etching of silicon (111). *Crystal Growth & Design, 9*(10), 4315–4323. https://doi.org/10.1021/cg900137h.

[48] Iqbal, S., et al. (2018). Highly-efficient low cost anisotropic wet etching of silicon wafers for solar cells application. *AIP Advances, 8*(2), 025223. https://doi.org/10.1063/1.5012125.

[49] Stefanescu, A., & Erk, H. F. (2001). *Alkaline etching solution and process for etching semiconductor wafers* (WO Patent No. 2001034877A1). https://patentscope.wipo.int/search/en/WO2001034877.

[50] Jones, A. R., & Coffman, Q. H. (1962). *Composition and process for etching magnesium* (US Patent No. 3053719A). https://worldwide.espacenet.com/patent/search/family/025114582/publication/US3053719A.

[51] Chen, L., et al. (2025). Corrosion of commercial pure titanium and two titanium alloys in extremely high-chloride and high-alkali seawater electrolysis environment. *Journal of Alloys and Compounds, 1020*, 179431. https://doi.org/10.1016/j.jallcom.2025.179431.

[52] Sutter, E. M. M., & Goetz-Grandmont, G. J. (1990). The behaviour of titanium in nitric-hydrofluoric acid solutions. *Corrosion Science, 30*(4–5), 461–476. https://doi.org/10.1016/0010-938X(90)90051-6.

[53] American Iron and Steel Institute. (2020). *Cleaning and descaling stainless steels: A designers' handbook series no. 9001*. Nickel Institute.

[54] Bright, R., et al. (2022). Bio-inspired nanostructured Ti-6Al-4V alloy: The role of two alkaline etchants and the hydrothermal processing duration on antibacterial activity. *Nanomaterials, 12*(7), 1140. https://doi.org/10.3390/nano12071140.