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Review

End-of-Life Chemistry of Polytetrafluoroethylene: From Destruction to Fluorine Reuse

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Abstract: Polytetrafluoroethylene (PTFE) is one of the most chemically and thermally resilient synthetic materials. That resilience underpins its value in aggressive service environments, but it also complicates end-of-life treatment. The central challenge is not simply to remove the parent polymer, but to determine where fluorine and carbon go after carbon-fluorine (C-F) bond cleavage and whether those products are benign, controllable or useful. This Review organizes the emerging chemistry of PTFE end-of-life management around five distinct endpoints, namely parent disappearance, bulk defluorination, fluorine mineralization, fluoride recovery and fluorine reuse. It compares high-temperature destruction, molten-hydroxide mineralization, reductive defluorination and mechanochemical conversion through a common set of descriptors spanning fluorine mass balance, sink quality, carbon fate, process intensity and deployment plausibility. A consistent picture emerges in which thermal routes remain the benchmark for feed tolerance and rapid elimination, but their practical value depends on suppressing incomplete-destruction products and coupling bond cleavage to robust fluoride capture. Milder chemical and solid-state routes show that PTFE can also be directed into defined mineral sinks or directly reusable fluorinating reagents, although they are often constrained by interfacial transport, crystallinity and feed heterogeneity. Future progress will depend on treating PTFE not only as a recalcitrant waste, but as a concentrated fluorine reservoir whose end-of-life chemistry must unite selective bond activation with accountable fluorine stewardship.

Keywords: polytetrafluoroethylene; fluoropolymer waste; end-of-life treatment; defluorination; fluoride recovery; fluorine recycling; mechanochemistry

1. Introduction

Polytetrafluoroethylene (PTFE) occupies an unusual position in materials chemistry. Few synthetic solids combine such low surface energy, chemical inertness, thermal stability and mechanical durability, which is why PTFE remains embedded in seals, membranes, wire insulation, non-stick coatings and chemically aggressive process hardware [1,2]. Yet the same durability that makes PTFE technologically valuable also places it at the centre of current debates around fluorinated materials. Within the wider universe of per- and polyfluoroalkyl substances (PFAS), fluoropolymers are increasingly discussed through

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the linked questions of terminology, essentiality, emissions and substitutability [3–10]. For high-performance sectors in energy, chemical manufacturing and transport, PTFE often remains difficult to replace [7,10]. Its end of life therefore poses a broader question than waste disposal alone: how should chemistry handle a material whose service value derives precisely from the molecular features that resist environmental and chemical breakdown [3,4,11–13]?

That question becomes sharper once PTFE is viewed as part of a product system rather than as a neat polymer powder. Landfilling merely stores a material engineered to resist decay, whereas thermal treatment can shift the burden downstream into gaseous fluorinated intermediates, hydrogen fluoride and secondary fluoride-containing waste streams [2]. In practice, PTFE seldom appears at end of life as a pure resin; it is more often present as coatings, membranes, seals, additives or thin functional layers dispersed through complex articles, where dilution, fillers and product architecture complicate collection, identification and treatment [3,4,11–13]. The life-cycle perspective summarized in Figure 1 therefore matters chemically as well as logistically. It links feedstock extraction, manufacture, use and waste management, while making clear that credible end-of-life chemistry must be judged not only by polymer disappearance, but by fluorine accounting, carbon fate and the quality of the sink into which fluorine is ultimately directed.

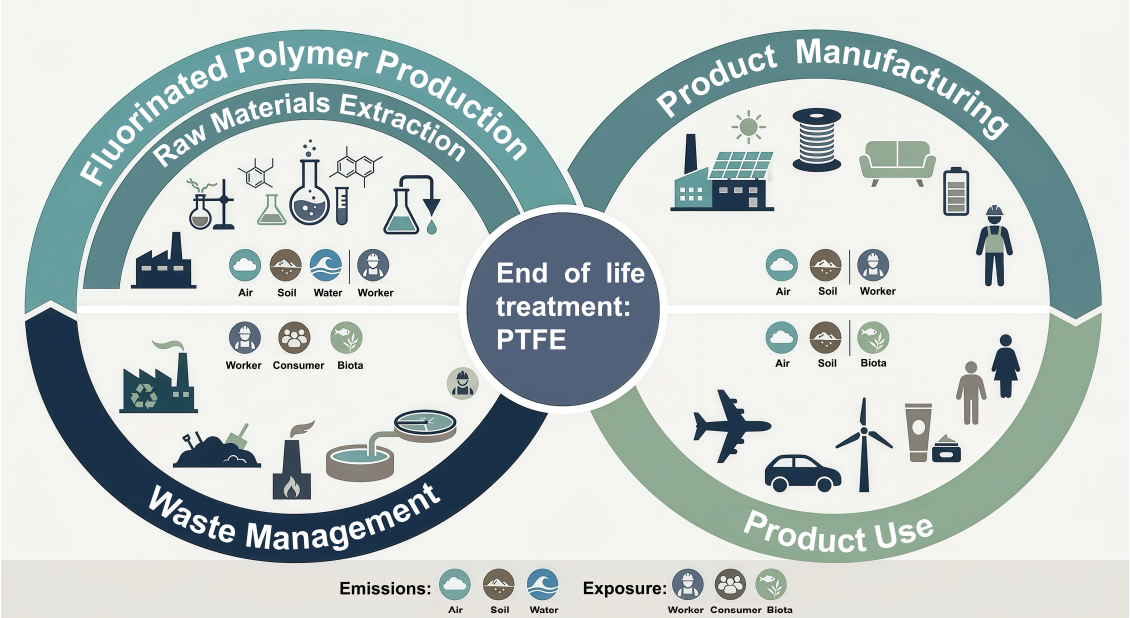

Figure 1. Lifecycle of fluorinated polymers from feedstock extraction and fluoropolymer production to product manufacturing, product use, and end-of-life management, together with the major emission and exposure compartments relevant to PTFE.

Against that background, PTFE has begun to function not merely as a disposal problem but as a chemically exacting test case for fluorine stewardship. High-temperature studies have clarified both decomposition pathways and product evolution, showing that the effectiveness of thermal treatment is governed not only by chain cleavage but by the fate and capture of fluorine once volatile intermediates have formed [14–37]. In parallel, chemistry-led routes have opened a complementary space in which bond activation is coupled directly to fluoride sequestration. Molten sodium hydroxide can mineralize PTFE to alkali fluoride that is subsequently precipitated as calcium fluoride (CaF_2) [38], a magnesium reagent has shown that room-temperature defluorination of solid PTFE is possible under remarkably mild conditions [39], and sodium dispersion has extended this logic to ambient conversion of PTFE into sodium fluoride (NaF) with fluoride recovery approaching quantitative levels [40]. Mechanochemical studies now push the argument further by demonstrating that fluoroplastics, including PTFE, can serve as fluorine donors for new synthesis rather than terminate as waste alone [41–54]. What gives these developments broader resource significance is that they begin to separate terminal sinks, in which fluorine is merely immobilized, from circular sinks, in which the recovered fluoride retains enough chemical quality to displace fresh fluorinating reagents.

These developments have altered the question that most usefully frames the field. Rather than asking simply whether PTFE can be destroyed, it is now more revealing to ask which endpoint should define success, parent disappearance, bulk defluorination, fluorine mineralization, controlled fluoride recovery, or direct fluorine reuse, and by what common set of criteria those routes can be compared. Accordingly, this

Review is organized around mechanisms, metrics, and endpoints rather than reactor type alone, on the premise that meaningful progress will require C-F bond cleavage to be coupled directly to a stable fluoride sink, structural barriers imposed by insolubility and semicrystallinity to be treated as central rather than secondary, and both fluorine and carbon to be followed to their final destinations.

2. A Framework for Judging End of Life PTFE Management

Any comparison of PTFE treatment routes becomes unstable the moment the endpoint is left implicit, because degradation, defluorination, fluorine mineralization, fluorine recovery, and fluorine reuse are still used with frustrating interchangeability even though they describe fundamentally different chemical achievements. A process may erase the parent polymer as an identifiable solid while still emitting fluorinated gases or leaving organofluorine in liquid or solid residues. It may release fluoride without placing fluorine into a benign or reusable sink. It may even approach complete defluorination while leaving carbon fate unresolved. These distinctions, now well recognized across the broader PFAS destruction, byproduct, and waste management literature, become especially important for PTFE, for which visual disappearance or simple mass loss can easily overstate genuine environmental control [52–56]. Placed against the wider PFAS classification framework (Figure 2a) and the partial overlap between PFAS, fluorinated gases, and fluoropolymer monomer building blocks (Figure 2c), PTFE is immediately seen as a chemically distinct but not analytically isolated case.

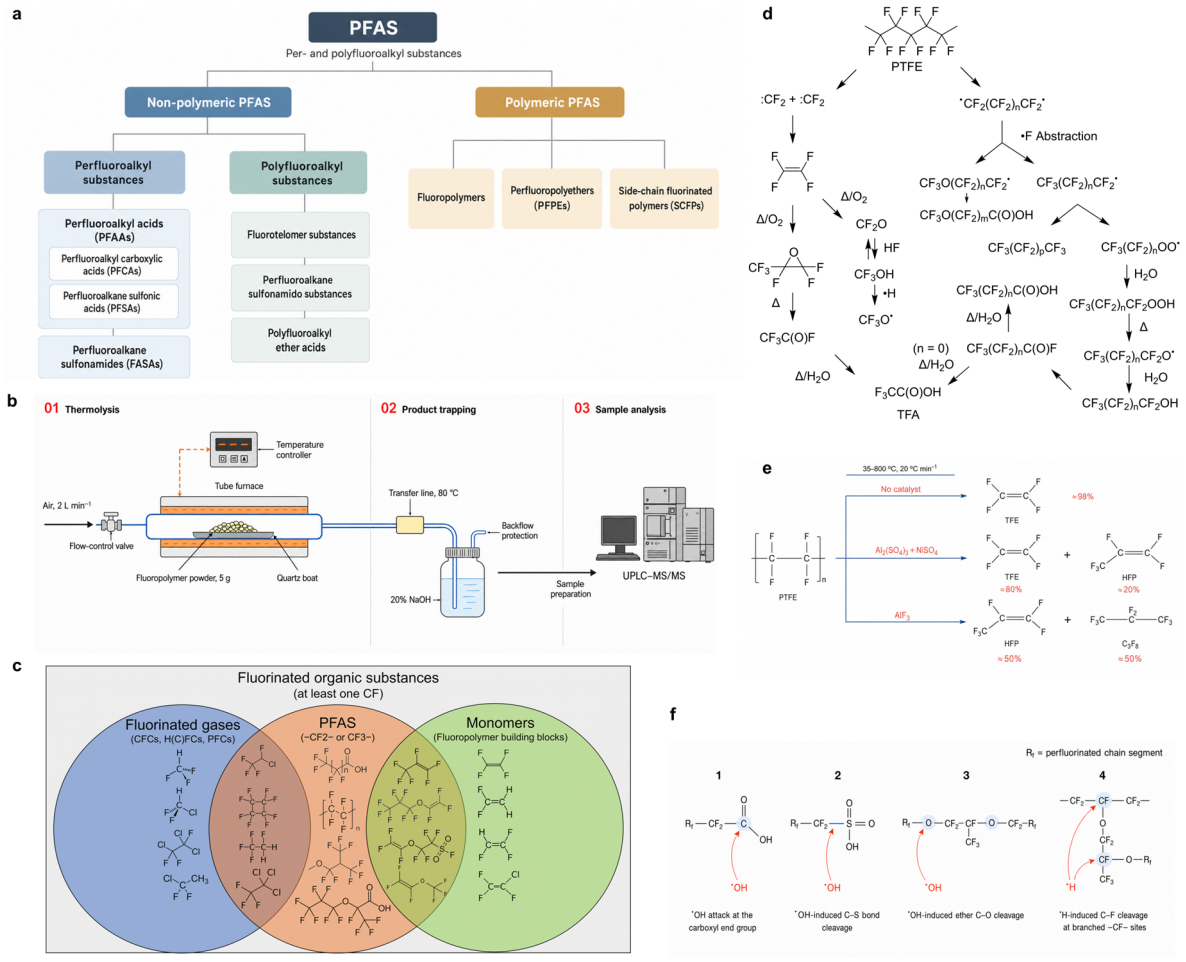

Figure 2. Conceptual context for judging PTFE within the broader PFAS and fluoropolymer landscape. (**a**) PFAS family classification. (**b**) Tubular-furnace thermolysis, product-collection, and analysis setup. (**c**) Overlap among fluorinated gases, PFAS, and fluoropolymer monomer building blocks, adapted from Ref. [5] under the Creative Commons Attribution 4.0 Unported License (https://creativecommons.org/licenses/by/4.0/) (**d**) Representative fluoropolymer thermolysis pathways leading to oxygenated products. (**e**) Effect of inorganic additives on PTFE pyrolysis product distribution. (**f**) Representative HO· attack mechanisms in perfluorosulfonic acid membranes.

For the purposes of this discussion, degradation denotes loss of the parent PTFE structure, bulk defluorination denotes cleavage of carbon-fluorine (C-F) bonds across the polymer mass rather than merely at the accessible surface, and fluorine mineralization denotes transfer of fluorine from PTFE into inorganic fluoride while leaving carbon fate to be accounted for explicitly as an independent axis. The more explicit phrase fluorine mineralization is used here as an operational definition to avoid implying complete mineralization of the carbon framework. Fluorine recovery sets a more demanding standard, since released fluoride must then be captured in a defined form such as calcium fluoride (CaF_2), sodium fluoride (NaF), potassium fluoride (KF), or another synthesis-relevant fluoride source rather than being dispersed across off-gas, scrubber liquor, and residual solids, while fluorine reuse raises that bar further still because the recovered fluorine must reenter chemical synthesis in a form that is not merely stable but functionally valuable [48–51]. The practical consequence is that parent disappearance, bulk defluorination, captured fluoride, and reusable fluoride quality must be treated as four related but distinct milestones.

Once the endpoint has been made explicit, fluorine mass balance becomes the first nonnegotiable metric, because PTFE management is, at its core, a problem of directing fluorine rather than merely erasing a visible substrate. Any study that reports only disappearance of the starting polymer, or only conversion of selected products, therefore remains intrinsically ambiguous. The broader PFAS destruction literature makes the point sharply, because targeted analysis can confuse transformation with true destruction and can miss volatile products of incomplete combustion, unidentified organofluorine in condensed phases, or fluoride that has simply been diverted into secondary waste streams [52–54]. Interlaboratory work on extractable organofluorine has reinforced how readily important fluorine pools can be overlooked when only targeted analytes are monitored [57], which is why fluorine accounting should, wherever relevant, encompass inorganic fluoride, gas-phase fluorinated products, and nontarget fluorine persisting in condensed phases. Surface-sensitive spectroscopies and microscopy remain mechanistically informative, but they cannot by themselves establish bulk conversion. Experimental designs such as the tubular-furnace thermolysis and sampling train shown in Figure 2b are informative for product identification, but they still resolve only part of the fluorine inventory unless gas, condensed, and residual phases are all reconciled.

PTFE routes are therefore most usefully compared through at least six descriptors, PTFE conversion, defluorination yield, fluorine recovery and speciation, carbon fate, process intensity, and deployment plausibility, because no single value captures the chemical or engineering meaning of success. Process intensity must absorb not only temperature, but also reagent consumption, electricity demand, corrosion burden, gas-cleaning requirements, milling energy, and residual handling, while deployment plausibility asks a stricter question than laboratory efficiency by probing whether the chemistry can tolerate realistic feeds, composite articles, background matrices, and scale-dependent engineering constraints. This systems perspective is entirely consistent with broader PFAS destruction, remediation, scale up, sustainability, and life-cycle analyses, all of which converge on the sobering conclusion that the most elegant bench chemistry is not automatically the most credible route at full scale [56–67]. The contrast with site-selective radical attack chemistry in perfluorosulfonic acid membranes (Figure 2f) is also instructive, because it shows that fluorinated polymers discussed under one PFAS umbrella can still fail through very different reactive motifs.

That framework becomes useful only once it is forced to do comparative work. Table 1 translates the six descriptors into a route-by-route synopsis. Neither device should be mistaken for a metaanalysis. Their purpose is instead to prevent the literature from retreating into serial description. The force of the framework becomes especially apparent as soon as one moves beyond pristine PTFE powder, because a route that performs beautifully on an idealized substrate may fail on aged gaskets, filled seals, expanded membranes, or mixed fluoropolymer waste, while a more energy intensive process may still be preferable if it accepts heterogeneous feeds and channels fluorine reproducibly into a controllable sink.

Table 1. Operational comparison of representative end of life PTFE management routes. PTFE conversion and defluorination should be read alongside fluoride sink quality, carbon fate, and evidence basis rather than as standalone success metrics [16,17,38–40,48–50].

Route Family	Representative Evidence	Parent Disappearance and Bulk Defluorination	Fluoride Sink and Quality	Carbon Fate	Process Intensity and Dominant Burdens	Evidence Basis and Feed Scope
High temperature destruction	Pilot incineration, plasma gasification [15–18]	High parent removal, bulk defluorination can be extensive when mineralizing conditions are sustained	Mainly hydrogen fluoride (HF) or inorganic fluorine in off gas, reusable fluoride only after scrubbing and further conditioning	CO_2 + volatile fluorocarbons if incomplete	Very high temperature, corrosion, refractory attack, scrubbing duty, byproduct analytics	Highest feed tolerance, includes PTFE and mixed fluoropolymer feeds
Molten hydroxide fluorine mineralization	Molten sodium hydroxide (NaOH) to calcium fluoride (CaF_2) [38]	High PTFE destruction and strong fluorine transfer to alkali fluoride and CaF_2	Defined mineral sink, circular reuse not yet central	Carbon tracked separately, carbonaceous residue not fully resolved	High temperature caustic medium, severe corrosion, washing, and salt load	Shown on defined fluoropolymer feeds, mixed product evidence still limited
Molecular or surface selective reductive routes	Magnesium reagent and related surface chemistries [39]	Mechanistically revealing but often surface biased and incomplete in bulk	Can generate chemically valuable fluoride species, but total bulk recovery is limited	Modified PTFE surface or partially defluorinated solid	Low temperature but specialized reagents, strict interfacial requirements, limited throughput	Evidence dominated by powders, films, and compositionally simplified substrates
Sodium dispersion	Ambient sodium dispersion in tetrahydrofuran (THF) [40]	Closest mild route so far to near bulk PTFE defluorination	NaF at high recovery, circular value depends on isolation and purity	Amorphous carbon rich residue	Ambient temperature but pyrophoric sodium, solvent management, mixing sensitive kinetics, solids separation	Strong on comminuted solids, heterogeneous product evidence remains sparse
Mechanochemical phosphate	K_3PO_4 and $K_4P_2O_7$ ball milling [48]	Near quantitative fluorine release under dry solid state conditions	KF or fluorophosphates, both chemically reusable	CO_2 + disordered or graphitic carbon	Mechanical energy, media wear, product conditioning, solid state separation	Dry solid feed, laboratory proof of principle
Mechanochemical potassium or sodium upcycling	KF and carbon composite or NaF and carbon routes [49,50]	Rapid PTFE defluorination with direct coupling to synthesis	Crude but chemically competent KF or NaF containing reagent pools	Reduced graphene oxide like or elemental carbon residues	Milling with reactive metals, jar wear, dust control, post milling conditioning	Includes thread seal tape and PTFE solids, sink presently oriented to specialty fluorination

3. High Temperature Destruction

High temperature destruction remains the reference route largely because it tolerates heterogeneous feeds and rapidly drives PTFE out of the macromolecular regime, although the underlying chemistry is considerably richer than the word incineration would suggest. Classical pyrolysis studies established that PTFE does not mineralize directly when first heated, but instead depolymerizes predominantly to tetrafluoroethylene under inert or reduced pressure conditions, while the surrounding gas atmosphere can inhibit, redirect, or oxidatively elaborate the decomposition sequence [23,24,68,69]. Subsequent kinetic and mechanistic work showed that this depolymerization is not a single step event but a temperature sensitive and transport sensitive process shaped by chain scission, unzipping, and gas phase secondary reactions [14,23,25–27], and comparative kinetics studies, including newer modelling analyses, reinforce that PTFE remains among the most thermally stable fluoropolymers, with a decomposition window that is both unusually narrow and unusually severe [22,25,26].

Later analytical studies sharpened the product picture by showing that, although tetrafluoroethylene is the dominant primary product under many pyrolytic conditions, perfluoropropene, octafluorocyclobutane, carbonyl fluoride, carbon tetrafluoride, and more oxidized species emerge once residence time, atmosphere, and diffusion limitations allow secondary chemistry to unfold [22,24,27,34,68–71]. The pathway map proposed for fluoropolymer thermolysis in Figure 2d remains useful precisely because it links these fragments to oxygenated products such as trifluoroacetic acid (TFA) under oxidizing conditions. That landscape becomes still more complex when feed heterogeneity is taken seriously, because thermogravimetric analysis coupled with Fourier-transform infrared spectroscopy (TG-FTIR) studies revealed that additives such as glass fibre, bronze, and carbon alter both the apparent stability of PTFE and the evolving gas-phase composition under nitrogen and air [72,73], while grain size and morphology likewise matter, underscoring that transport can be as consequential as intrinsic bond strength [37]. Intimate mixing with metal sulfates, fluorides, and oxides shifts onset temperatures and product selectivity still further [74,75], and the additive effects summarized in Figure 2e make the same point graphically. These observations are more than mechanistic detail, since end-of-life PTFE seldom enters a furnace as a pristine powder, but instead arrives embedded in filled, aged, or composite articles whose local chemistry and mass transport are inseparable from their decomposition behaviour.

What modern simulations and reactive-atmosphere experiments now provide is a bridge between those macroscopic observations and microscopic pathway assignment. Reactive force field (ReaxFF) studies reproduce a sequence of random backbone cleavage, beta-scission-driven unzipping of C_2F_4 units, and secondary fluorocarbon formation [14], while plasma gasification experiments show that oxygen and steam access distinct pyrolysis-oxidation and fluorine-abstraction/hydrolysis routes, with mixed O_2 and H_2O atmospheres increasing the fraction of inorganic fluorine in the gas phase and enabling substantial gaseous fluorine recovery within minutes [15]. The generic degradation network compiled in Figure 3b is useful here because it makes explicit how depolymerization, cyclization, oxidation, and hydrolysis compete once PTFE fragments enter the gas phase. High-temperature treatment therefore succeeds only when atmosphere design suppresses persistent fluorocarbon intermediates while simultaneously promoting transfer of fluorine into capturable inorganic form.

Viewed from the standpoint of process design, the central challenge is less chain scission itself than fluorine capture, because under representative waste-incineration conditions PTFE is transformed mainly to hydrogen fluoride (HF) and carbon dioxide (CO_2), with little evidence for the targeted PFAS set in flue gas [16]. A later pilot-scale study on mixed fluoropolymer feeds again reported negligible targeted PFAS and fluoropolymer reduction rates above 99.99%, yet explicitly argued that destruction efficiency is not a valid surrogate for mineralization [17]. The furnace and sampling train used in the recent byproduct study (Figure 3a) make the same systems point experimentally, because reactor conditions and downstream collection media must be interpreted as one coupled analytical unit rather than as separate steps. That distinction is fundamental, since reactor walls, ash, scrubber liquors, and downstream gas-cleaning units all participate in fluorine redistribution, so that apparent disappearance of PTFE can easily coexist with incomplete fluorine accounting.

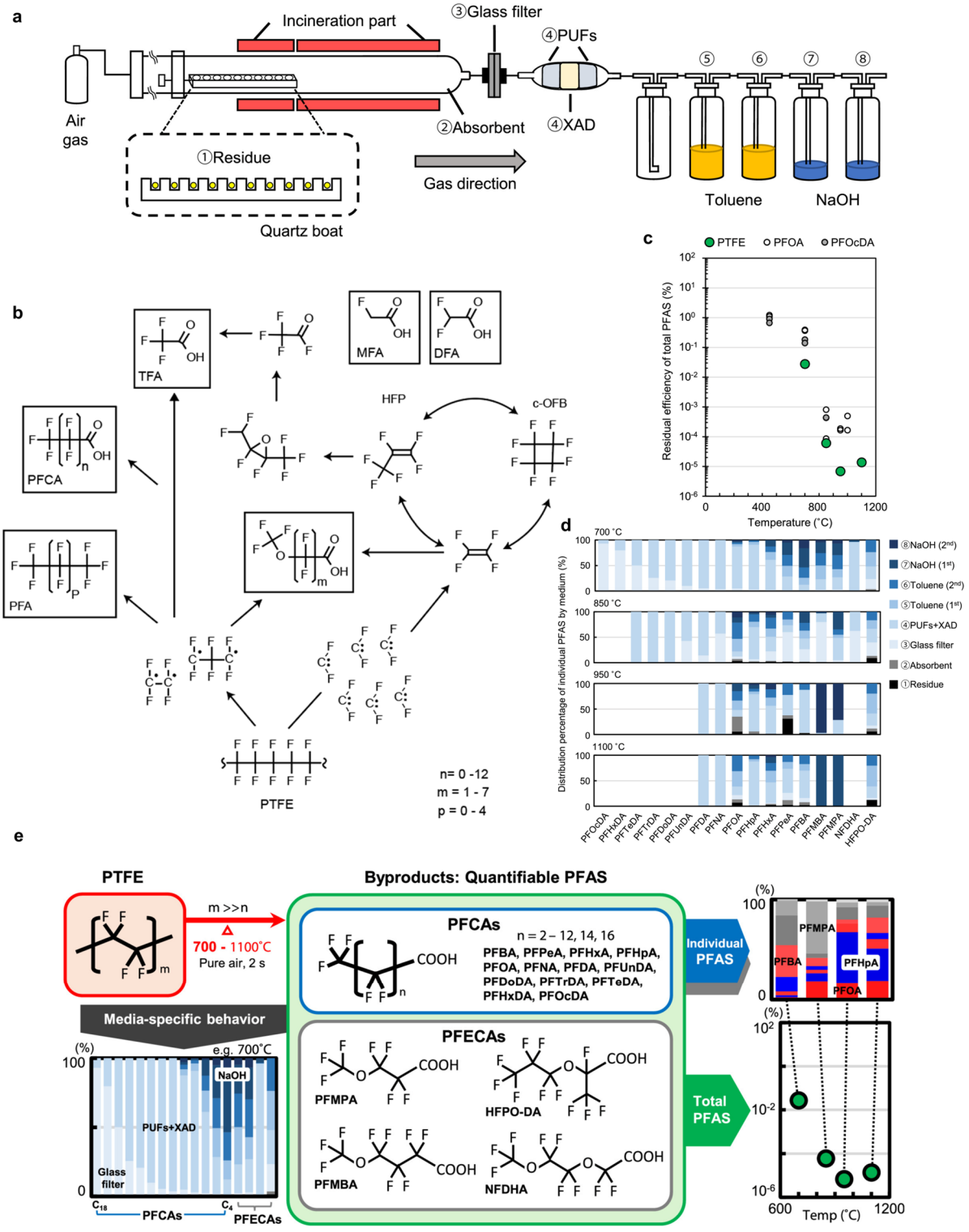

Figure 3. Representative evidence for PTFE incineration and byproduct control. (**a**) Laboratory-scale control furnace and sampling train, adapted from Ref. [18]. (**b**) Proposed PTFE thermal degradation network. (**c**) Residual efficiency of total PFAS after PTFE incineration as a function of temperature, adapted from Ref. [18]. (**d**) Distribution of individual PFAS across sampling media after PTFE incineration, adapted from Ref. [18]. (**e**) Comparative evaluation of quantifiable PFAS byproducts from PTFE incineration, adapted from Ref. [18]. (**a**,**c**,**d**,**e**) are adapted under the Creative Commons Attribution 4.0 International License (https://creativecommons.org/licenses/by/4.0/).

The need to treat off-gas control as part of the chemistry rather than as an afterthought has, in fact, been visible for decades in the toxicology literature. Historical studies on PTFE pyrolysis products identified toxic particulate emissions, carbonyl fluoride, and silicon tetrafluoride-related hazards, and showed that biologically significant exposures could arise even when nominal temperatures remained below the most

severe combustion regime [28–33]. More recent combustion- and fire-relevant measurements continue to detect HF formation close to the reacting PTFE surface and show that oxidizer composition shapes toxicant formation pathways [35]. Temperature windows matter as well, since the most recent targeted byproduct study quantified perfluorocarboxylic acid (PFCA) and perfluoroether carboxylic acid (PFECA) generation during PTFE incineration and found that total PFAS byproducts were strongly suppressed above 850 °C [18]. That temperature dependence is visible in Figure 3c,e, while Figure 3d,e show that the residual PFAS burden is redistributed strongly across collection media rather than appearing in a single sink. Model-compound work and fluoropolymer thermolysis studies suggest that TFA- or PFCA-related products can arise under suboptimal conditions [19–22,34,36], again pointing to the necessity of complete mineralization and downstream capture rather than simple polymer disappearance.

High temperature PTFE management is therefore best understood not as a single destruction step but as an integrated reactor and gas cleaning system whose environmental credibility rests on complete fluorine accounting, robust HF or fluoride capture, and tight control over products of incomplete destruction. Seen in this light, high temperature treatment remains indispensable because it is the most feed tolerant route and the current benchmark for rapid PTFE elimination, even though its real limitation is not simply energy demand but the requirement that bond cleavage, fluorine capture, byproduct suppression, refractory integrity, and gas cleaning performance all succeed together. What often makes the route look deceptively simple is merely that many of its burdens are counted downstream rather than at the moment of C-F cleavage. That same requirement, direct coupling of C-F scission to a robust fluoride sink, reappears in chemically sharper form in fluorine mineralization and reductive defluorination routes.

4. Chemical Fluorine Mineralization and Reductive Defluorination

Chemical routes render explicit what high temperature destruction often leaves only partially resolved, because the central question is not merely whether PTFE fragments, but whether C-F cleavage is coupled immediately to a well defined fluoride sink. Older reagent assisted high temperature studies had already shown that PTFE can be diverted from simple depolymerization into more structured product manifolds. In supercritical water with $Ca(OH)_2$, PTFE was converted into amorphous carbon nanospheres [76], while metallic magnesium in supercritical CO_2 drove defluorination to carbon microsphere chains [77]. Related conversion work used PTFE as a precursor to porous carbon, nanoporous carbon from halogen containing plastic waste, and even silicon carbide nanocrystals [78–81], illustrating that fluorine rich polymer waste can indeed be redirected into useful carbonaceous or ceramic products under carefully designed conditions, even if these studies placed greater emphasis on the carbonaceous product than on fully quantified fluoride recovery.

Within this landscape, molten sodium hydroxide (NaOH) remains the clearest fluorine mineralization benchmark because fluoride recovery sits at the centre of the process rather than emerging as a downstream consequence. Yanagihara and Katoh used a two-step protocol in which PTFE was first mineralized to soluble alkali fluoride in molten hydroxide and then converted to calcium fluoride (CaF_2) by addition of calcium chloride ($CaCl_2$) [38]. With excess NaOH at 500 °C, PTFE gave a high CaF_2 yield, whereas substitution of potassium hydroxide (KOH) lowered performance markedly [38]. Within the cross-route comparison shown in Figure 4d, this molten-hydroxide route remains the clearest benchmark for coupling bond cleavage directly to a defined mineral sink. The conceptual importance of this route lies in the fact that bond activation and fluoride sequestration occur within the same chemical environment, thereby defining a stringent benchmark against which later low-temperature strategies must be judged, since any milder route must show not only PTFE disappearance, but an equally credible destination for liberated fluorine. At the same time, the very design feature that makes the chemistry convincing also seeds its deployment liabilities, because the treatment medium doubles as fluoride sink and thereby brings corrosion management, caustic handling, washing, and salt load directly into the process core.

The logic of low temperature reductive defluorination long predates the contemporary language of fluorine circularity. Bondability treatments and early surface conditioning protocols already showed that alkali metal based reduction could activate accessible PTFE domains and make the polymer chemically or mechanically more tractable [82–85], while sodium atoms, benzoin dianion, and related reductive systems established that PTFE could be chemically modified under conditions far milder than furnace based destruction [82,86,87]. Other studies pushed the chemistry towards more unusual outcomes, including partial alkylation, conducting PTFE derived materials, and carbonization through radical anion routes [75,86,88,89], and additive controlled magnesium reduction, sodium naphthalenide diglyme etching, and electrochemically

generated radical anion systems refined that picture by showing that reagent speciation, counterions, and interfacial control are central to any mild PTFE chemistry [39,90–92].

What more recent studies have changed is the framing of these reactions, because PTFE is now being treated less as a merely modifiable surface than as a potential fluorine resource. The magnesium reagent reported by Sheldon and co-workers isolates a separable molecular magnesium fluoride at room temperature and reuses that fluoride in downstream fluorination chemistry [39]. The room-temperature PTFE transformation and the companion density functional theory (DFT) analysis are shown in Figure 4a,b. But the same study is equally revealing for what it says about limitation, since nuclear magnetic resonance (NMR), X-ray diffraction (XRD), and scanning electron microscopy (SEM) all indicated that most of the bulk polymer remained unchanged and that amorphous surface regions were the most reactive domains [39]. Herlem and co-workers later generated lithium alkylamides in situ at 20 °C, enabling direct PTFE defluorination and amination with lithium fluoride (LiF) precipitation as the only byproduct [93]. Here the evidentiary asymmetry becomes important, because most mild routes still derive their strongest data from powders, etched films, or other compositionally simplified solids rather than from filled seals, expanded PTFE membranes, or aged coated articles. Together these studies show that mild PTFE chemistry can do more than etch the surface, while also making clear that the outcome depends critically on how electrons are delivered to the solid and how rapidly fluoride is trapped once released.

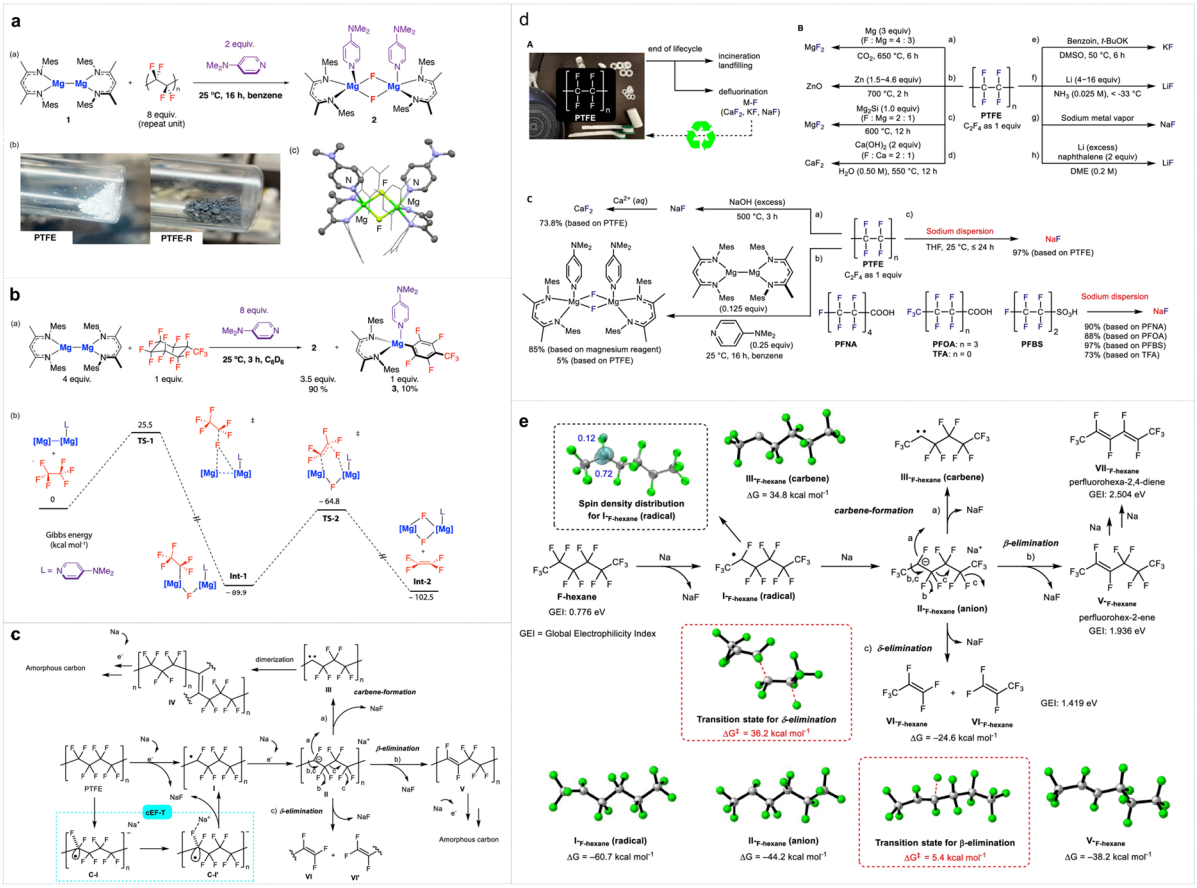

Figure 4. Chemical fluorine mineralization and reductive defluorination routes for PTFE. (**a**) Room-temperature reaction of a magnesium reagent with PTFE, together with photographs of PTFE and reacted PTFE (PTFE-R) and the isolated complex, adapted from Ref. [39]. (**b**) Reaction with a model perfluoroalkane and the associated DFT pathway, adapted from Ref. [39]. (**c**) Proposed sodium-mediated PTFE defluorination mechanism, adapted from Ref. [40]. (**d**) Lifecycle framing and state-of-the-art PTFE defluorination approaches, adapted from Ref. [40]. (**e**) Perfluorohexane-based calculations used to rationalize sodium-mediated defluorination, adapted from Ref. [40]. All Panels are adapted under the Creative Commons Attribution 4.0 International License (https://creativecommons.org/licenses/by/4.0/).

The sodium dispersion route provides the clearest demonstration so far that mild chemistry can approach process-relevant fluorine recovery from PTFE. Under optimized conditions in tetrahydrofuran (THF) at ambient temperature, Araki and co-workers obtained up to 97 to 98% NaF from PTFE [40], yet the

optimization data show why this result should not be compressed into a single headline number, since larger PTFE particles remained reactive but required longer times, stirring speed was critical, the formulation of the dispersion strongly affected yield, and radical trapping suppressed the reaction [40]. The proposed sodium-mediated pathway and the perfluorohexane-based calculations in Figure 4c,e reinforce that immediate NaF formation is coupled to carbonization rather than to simple clean unzipping. The residue was transformed largely into an amorphous, carbon-rich material, with only a small amount of unreacted PTFE still detectable, making the study valuable not merely as a proof of concept but as a kinetic map of how interfacial renewal, electron transfer, and immediate NaF formation become inseparable parts of the same problem. Set beside the broader route map in Figure 4d, sodium dispersion is notable because it exchanges thermal severity for a much sharper burden profile centred on reagent safety, solvent control, mixing-sensitive kinetics, and solids separation [40].

Across low-temperature routes, the recurring barrier is not nominal bond strength alone but access, because PTFE is a semicrystalline, insoluble solid and defluorination begins only where electrons, radicals, or nucleophiles can reach and where new surface is continuously exposed. Related fluoropolymer studies reinforce the point. Superheated water mineralization of fluoroelastomers in KOH and subcritical water mineralization of poly(tetrafluoroethylene-co-hexafluoropropylene) (FEP) in KOH both achieved very high fluoride yields [94,95], while the recent demonstration of complete PFAS defluorination by photocatalytic reduction in water shows how decisively reaction medium, reductant delivery, and product trapping can reshape the apparent limits of C-F bond activation in aqueous systems [96]. For PTFE itself, however, an equally effective water-based analogue has not yet emerged, and the more uncomfortable lesson is that most low-temperature evidence still arises from neat powders or otherwise simplified substrates rather than from heterogeneous product forms. Mild chemistry succeeds only when C-F cleavage, interfacial transport, and immediate fluoride capture are engineered together, which is precisely why mechanochemical strategies have become so attractive, since they force contact creation and bond activation in the solid state rather than leaving both to sluggish solution transport.

What this means in deployment terms is that the low temperature routes do not remove system burdens so much as redistribute them. Molten hydroxides push difficulty into corrosion and salt management, sodium dispersion displaces it into reagent safety, solvent control, and solids separation, and surface selective reductive routes remain mechanistically illuminating but will remain deployment limited unless they can demonstrate bulk conversion in the presence of fillers, binders, ageing, and heterogeneous contaminants [38–40,82–93,96].

5. Core Mechanisms of PTFE C-F Bond Activation

The C-F bond energy in PTFE molecules is approximately 485 kJ/mol; combined with the polymer's semi-crystalline structure and enhanced inertness, this makes activating carbon-fluorine bonds a core chemical challenge in end treatment. The existing mainstream disposal technologies follow three core mechanisms, based on differences in driving forces and reaction phases: thermally driven degradation, liquid-phase reduction/alkali mineralization, and mechanochemical solid-phase activation. The differences in bond-fracture paths, intermediate-product evolution laws, and fluoride fate directly determine the application boundaries and engineering bottlenecks of each technology.

5.1. Thermal Degradation Mechanism

The activation of C-F bonds in PTFE under thermal drive follows a stepwise evolution path of "depolymerization, secondary reactions, and deep mineralization", and the complete reaction network is shown in Figures 2d and 3b. In an inert atmosphere, PTFE first undergoes depolymerization via random breakage of the main chain, releasing tetrafluoroethylene monomer via a β-scission mechanism, which is the initial primary reaction of thermal degradation. As the temperature increases or the residence time lengthens, the released gaseous monomers will undergo further cyclization and dimerization, producing perfluorohydrocarbon intermediates such as octafluorocyclobutane and perfluoropropylene. In an oxidizing atmosphere, the aforementioned fluorine-containing intermediates undergo oxidation and hydrolysis with oxygen and water vapor, gradually generating carbonyl fluoride and trifluoroacetic acid (TFA), and subsequently forming PFAS by-products such as perfluorocarboxylic acid (PFCA) and perfluoroether carboxylic acid (PFECA). The amount generated is highly correlated with temperature and atmospheric composition (Figure 3c–e). When the temperature is above 850 °C and the residence time is sufficient, the vast majority of fluorine-containing intermediates can be completely oxidized, and the carbon

skeleton is ultimately converted into CO_2. Fluorine primarily enters the gas phase as HF and must be captured by the tail gas washing unit. If the temperature is insufficient or the atmosphere is not properly controlled, incomplete degradation products will escape with the flue gas, causing a risk of secondary pollution.

5.2. Liquid Phase Reduction and Alkali Mineralization Mechanism

The activation of C-F bonds in the liquid phase and in molten alkali systems is mainly achieved through two mechanisms: nucleophilic attack and single-electron transfer. The molten alkali mineralization route uses high-temperature molten NaOH/KOH as the reaction medium, and OH- can promote interfacial defluorination and mineralization in molten alkali, likely through coupled nucleophilic/ionic pathways. The released fluoride is captured by the alkali metal cation to form a soluble alkali metal fluoride, which can subsequently be converted into a stable CaF_2 mineral phase via calcium salt precipitation, thereby achieving terminal fixation of fluorine. The mild liquid-phase reduction pathway is driven by electron transfer as the primary driving force: the magnesium reagent system (Figure 4a,b) transfers a single electron to the C-F bond on the PTFE surface at accessible PTFE interfaces by the magnesium reagent, generating carbon radical intermediates. With the C-F bond cleavage, liberated fluoride is trapped by magnesium-containing species to form stable Mg-F products. This reaction can occur at room temperature but is limited by mass transfer and acts only on the amorphous region of the polymer surface. The sodium dispersion system (Figure 4c,e) employs a highly active sodium dispersion phase as an electron donor, thereby triggering C-F bond cleavage via free-radical-anion mechanisms. During the reaction, fluoride released during C-F bond cleavage is captured as NaF, which precipitates, while the carbon skeleton simultaneously carbonizes to form an amorphous, carbon-enriched residue. Both reduction routes rely on the thermodynamic driving force of "in-situ precipitation of fluoride salts" to pull the reaction forward, but their reaction depth is highly dependent on the effective contact between the electron donor and the polymer surface.

5.3. Mechanochemical Solid Phase Activation Mechanism

The mechanochemical pathway achieves solid-phase activation of C-F bonds under solvent-free conditions via mechanical force. The core mechanism comprises three steps: lattice defect induction, continuous interface refreshing, and in situ fluorine fixation. During ball milling, continuous impact and shear can damage the crystalline structure of PTFE, generating numerous lattice defects and unsaturated active sites within the particles. At the same time, the particles are continuously ground, exposing fresh reaction interfaces and providing mass-transfer channels for solid-phase reactions, thereby partly mitigating the mass-transfer limitations imposed by PTFE insolubility and semicrystallinity. Taking the phosphate ball milling system as an example (Figure 5a), co-grinding reagents such as K_3PO_4 or $K_4P_2O_7$ achieve intimate solid-solid contact with newly generated PTFE interfaces under mechanical force. The C-F bond at the newly formed interface breaks in the locally high-energy environment, and the released fluoride is captured by potassium- and phosphate-containing species to form KF or a fluorophosphate, thereby achieving in situ fixation of fluorine. The carbon skeleton is partially converted into CO_2 and partially forms disordered or graphitized carbon under the combined action of mechanical force and an oxidative environment. This mechanism does not require high temperatures or organic solvents and can directly convert PTFE into reusable fluorine-source reagents. However, reaction uniformity and product purity are significantly affected by wear in the grinding medium and by the uniformity of material mixing.

5.4. Inhibition Effect of Structure and Impurities on C-F Bond Activation

The semi-crystalline structure of PTFE and filler impurities in actual waste materials are common bottlenecks that limit the activation efficiency of C-F bonds across various routes, thereby confirming the core assertion that material accessibility is the core bottleneck. From the perspective of the polymer's intrinsic structure, the molecular chain arrangement in the PTFE crystalline region is highly regular and compact, making it difficult for reagent molecules, electrons, and reactive free radicals to penetrate into the bulk phase. The vast majority of reactions can only occur in the amorphous region and defect sites on the surface. This is also the fundamental reason why mild liquid-phase routes commonly exhibit surface bias and are difficult to achieve deep defluorination in bulk. From the perspective of actual waste properties, industrial PTFE products often contain fillers such as glass fiber, bronze, and carbon black. On the one hand, fillers can dilute effective reaction sites and hinder the diffusion of active species into the polymer interior; on the other hand, some fillers may consume reaction reagents or interfere with heat conduction and the transfer of mechanical forces, thereby decreasing reaction efficiency and product selectivity. Whether it is

thermal degradation, liquid-phase reduction, or mechanochemical routes, the core of their technological optimization revolves around enhancing the effective contact between active species and C-F bonds, and material accessibility has therefore become the core limiting factor that runs through all PTFE end treatment technologies.

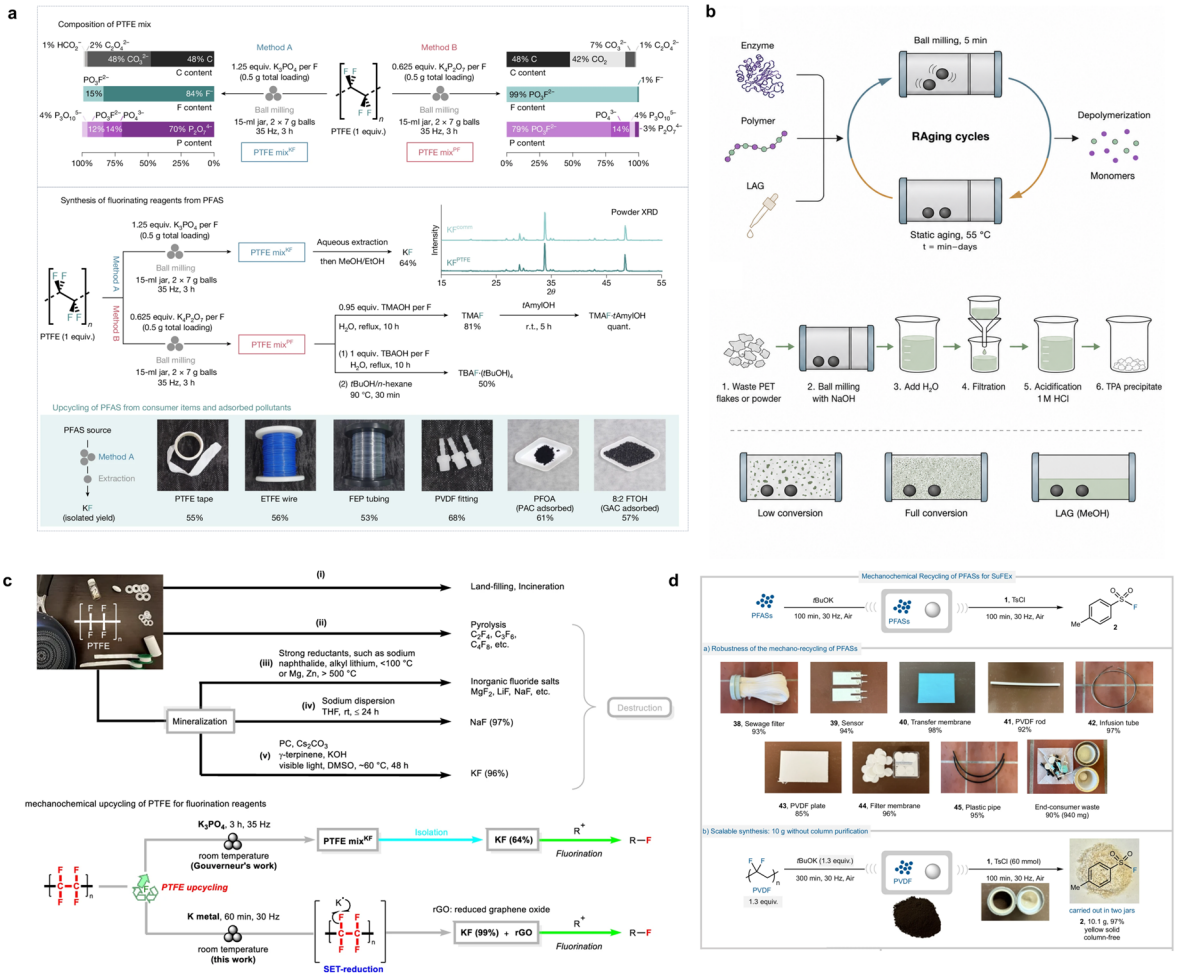

Figure 5. Mechanochemical pathways for PTFE destruction, fluoride recovery, and fluorine reuse. (**a**) Phosphate-enabled mechanochemical conversion of PTFE and other PFAS into reusable fluoride sources, adapted from Ref. [48]. (**b**) Representative solid-state depolymerization and hydrolysis workflows, including reactive-ageing (RAging)-assisted biopolymer depolymerization and mechanochemical/vapor-assisted polyethylene terephthalate (PET) hydrolysis. (**c**) Comparison of PTFE mineralization and upcycling routes: (**i**) landfilling or incineration, (**ii**) pyrolysis to fluorocarbon products, (**iii**) mineralization with strong reductants, (**iv**) sodium-dispersion mineralization, and (**v**) visible-light-assisted defluorination, together with mechanochemical conversion of PTFE into fluorinating reagents, adapted from Ref. [49] under the Creative Commons Attribution-NonCommercial-NoDerivatives 4.0 International License (https://creativecommons.org/licenses/by-nc-nd/4.0/). (**d**) Mechanochemical generation of sulfur(VI) fluoride exchange (SuFEx) hubs and gram-scale defluorination of poly(vinylidene fluoride) (PVDF)/PFAS-derived feeds, adapted from Ref. [51]. (**a**,**d**) are adapted under the Creative Commons Attribution 4.0 International License (https://creativecommons.org/licenses/by/4.0/).

6. Mechanochemistry and Pathways to Fluorine Reuse

Mechanochemistry speaks directly to the central kinetic obstacle identified above, because ball milling does not rely on dissolving PTFE or sustaining reagent transport through a bulk liquid phase, but instead repeatedly creates fresh interfaces, defects, and transient reactive states within an insoluble solid. More broadly, ball milling has evolved from a niche degradation method into a general platform for polymer recycling and upcycling, with two advantages that are especially relevant here: solvent demand can be minimized, and the hardware itself is not intrinsically confined to benchtop scale [41,42]. Representative solid-state depolymerization and hydrolysis workflows from reactive ageing (RAging) and polyethylene

terephthalate (PET) valorization studies (Figure 5b) [97,98] provide a useful mechanistic backdrop, because they show how repeated milling and ageing can replace solution transport with contact renewal and solid-state activation. Mechanochemical fluoropolymer chemistry also predates the present PTFE upcycling wave, since poly(vinylidene fluoride) (PVDF) had already been shown to undergo solid-state reaction with NaOH, and more recently Lewis-acid-induced milling has converted PVDF into valuable inorganic and carbonaceous products [52,53]. That broader context matters because it shows that fluoropolymer bond activation can be driven in the solid state without requiring solubilization of the substrate.

The enabling principles for PTFE emerged first from non-PTFE PFAS work, where early mechanochemical studies showed that comilling chemistry is decisive, with potassium hydroxide (KOH) promoting destruction where lithium hydroxide (LiOH), sodium hydroxide (NaOH), and caesium hydroxide (CsOH) did not [43]. Planetary ball mill treatment of perfluorooctanesulfonic acid (PFOS) and perfluorooctanoic acid (PFOA) amended sand then demonstrated very high concentration reduction in dry media, while also revealing two constraints that would later matter for fluoropolymers more broadly, since water suppresses destruction and fluoride recovery depends strongly on the comilling reagent [44]. The field subsequently advanced along two applied directions, with horizontal ball mill studies demonstrating remediation from litre to industrial scale [45,47], while complex matrices such as aqueous film-forming foam (AFFF) concentrates, contaminated soils, sediments, and sorbent-bound PFAS were shown to be amenable to mechanochemical destruction, and piezoelectric boron nitride enabled complete destruction and near-quantitative defluorination of solid PFOA and PFOS without caustic additives [46,47,99,100]. These studies did not solve PTFE by themselves, but they defined the operating variables that matter most, contact renewal, comilling chemistry, matrix water, sorbent environment, and scale-dependent energy delivery.

Against that background, phosphate-enabled mechanochemical mineralization of PTFE marked a turning point. The phosphate-enabled PTFE chemistry shown in Figure 5a makes this transition especially clear. Ball milling PTFE with K_3PO_4 or $K_4P_2O_7$ delivered close to quantitative fluorine release, although the endpoint depended strongly on the activator [48]. K_3PO_4 favoured fluoride-rich mixtures, whereas $K_4P_2O_7$ favoured fluorophosphate formation, and KOH, despite its effectiveness for some small-molecule PFAS under milling, released little fluoride from PTFE [48]. Carbon did not vanish from the system, but its fate became chemically legible, appearing as a combination of CO_2, disordered or graphitic carbon, and defined fluoride-containing salts. At that point mechanochemistry crossed an important threshold, because PTFE was no longer merely abraded or superficially modified, but was being pushed into near-quantitative fluorine recovery under solvent-free solid-state conditions.

The deeper conceptual shift, however, lay not simply in fluoride release but in reagent generation. Within the phosphate platform, PTFE-derived KF and fluorophosphate products were isolated and reused in fluorination chemistry, including sulfur-fluorine (S-F) bond formation and copper-mediated aryl fluorination [48]. Figure 5a captures that dual role of the mechanochemical product stream as both a destruction endpoint and a reagent pool. Once a crude destruction mixture functions as a reagent pool, end-of-life treatment ceases to be merely terminal and becomes part of synthesis design. The potassium-mediated PTFE route reported by Hattori and co-workers pushed this logic further towards direct use by converting PTFE, including commercial thread seal tape, within an hour into a KF and carbon composite derived from PTFE that could be used directly in fluorination reactions without prior purification [49]. The comparison in Figure 5c is useful because it places that strategy alongside higher-temperature mineralization and sodium dispersion rather than treating mechanochemistry in isolation. Lowe and co-workers reached a related destination through sodium-mediated reductive mechanochemistry, where ball milling PTFE with sodium metal at room temperature and without organic solvent generated a benign mixture of carbon and NaF in very high yield, and the resulting fluoride was upcycled in situ to sulfonyl fluoride and acyl fluoride products in excellent yields [50]. Recent single-pot work suggests that the concept can be taken further still, with PTFE and other PFAS used directly as fluorinating agents in a closed-loop mechanochemical workflow [51], a shift that has now been recognized explicitly in perspective-style commentary on mechanochemical fluorine upcycling [54]. Figure 5d extends the argument to closed-loop, sulfur(VI) fluoride exchange (SuFEx)-oriented workflows and gram-scale defluorination.

Once PTFE is treated as a fluorine feedstock rather than as a disposal burden, the benchmark for success changes accordingly. Defluorination percentage remains necessary, but it is no longer sufficient, because the strongest routes now distinguish themselves by what they do with liberated fluorine, how much separation they require, and whether their reagent systems are recoverable or scalable. The phosphate route offers recoverable phosphate salts and multiple fluorine containing outputs [48]. The potassium route tolerates real PTFE articles and uses the crude PTFE derived KF and carbon mixture directly [49]. The

sodium route simplifies the reagent set while coupling NaF formation to in situ product synthesis [50]. Set against the broader mechanochemical PFAS literature, this progression from destruction of contaminated solids to deliberate design of fluorine economy is striking [41–54,99,100].

What remains less settled is the class of sink that these chemistries are actually establishing. CaF_2, NaF, and KF should not be treated as interchangeable successes, because they occupy different system roles. CaF_2 is a terminal mineral sink whose value lies in stable sequestration and possible reintegration into mineral processing value chains. NaF and KF are intermediate chemical sinks whose circular value depends on impurity tolerance, isolation burden, and downstream demand. Fine chemical fluorination products demonstrate that reagent quality can survive the waste to reagent transition, yet they remain proof of concept outlets unless the scale of the consuming chemistry can plausibly match the scale of PTFE bearing waste [38,48–51,54]. The published upcycling demonstrations presently operate from millimole to decagram scales and target specialty fluorination chemistry, so a likely mismatch persists between the volumes represented by diffuse PTFE waste streams and the sinks available in synthesis oriented studies [49–51,54]. Table 2 therefore operationalizes fluorine-sink quality by separating terminal sequestration, industrial feedstock, and fine-chemical reagent grades.

Table 2. Functional grading of recovered fluorine sinks from PTFE end-of-life processes.

Functional Grade	Typical Products	Main Quality Requirement	Impurity Tolerance	Reuse Implication
Terminal sequestration grade	CaF_2; scrubber-derived mineral salts	Phase stability and low leachability rather than reagent purity	Relatively high	Disposal, long-term immobilization, or mineral-chain reintegration
Industrial feedstock grade	NaF, KF, mixed alkali fluorides	Controlled inorganic impurities and low residual organofluorine	Moderate	Requires purification or conditioning before use
Fine-chemical reagent grade	Dry KF/NaF-containing reagent pools	Moisture, metal, and carbon impurities compatible with the target reaction	Low or route-specific	Limited to specialty fluorination unless scale and purity are demonstrated

Even so, the field has not yet settled into a single dominant logic. Carbon fate still varies across systems and remains less standardized than fluorine accounting, with reported endpoints including disordered carbon, reduced graphene oxide like solids, and elemental carbon [48–50]. Reagent choice likewise imposes genuine tradeoffs, since alkali metal routes offer speed and synthetic immediacy but raise handling questions, whereas phosphate routes provide recoverable activators and chemically versatile products at the cost of a more complex product inventory. Nor should the solid state setting be mistaken for a route without infrastructure burdens, because milling media wear, jar contamination, dust control, heat management, and post milling separation of salts, coreagents, and carbon residues all enter once the chemistry is scaled or applied to heterogeneous solids [41,42,45,47,99,100]. More fundamentally, the non PTFE mechanochemical literature continues to show that performance is highly contingent on local environment, KOH succeeds where other hydroxides fail, water suppresses degradation, and sorbent assisted strategies can raise throughput dramatically [43,44,46,47,99,100]. Mechanochemical PTFE management will therefore be determined not only by bond dissociation energetics, but by how intelligently milling media, coreagents, sorbents, and product sinks are integrated. Table 3 makes those deployment asymmetries explicit by separating evidence basis, dominant liabilities, and likely sink class.

As shown in Table 3, through a horizontal comparison of the four dimensions of real raw material verification, industrial core shortcomings, fluorine sink types, and core unresolved bottlenecks, the industrial positioning differences of five types of PTFE end treatment technologies, namely high-temperature destruction, molten alkali mineralization, mild reduction liquid-phase routes, sodium dispersion defluorination, and mechanochemical fluorine recovery, can be systematically clarified. This clearly reveals the significant mismatch between laboratory conversion efficiency and industrial deployability.

Among them, the high-temperature destruction route has the strongest real raw material verification foundation among the five types of processes, and has completed pilot studies on PTFE incineration and

mixed fluoropolymers, which can directly accept industrial fluorine-containing waste with complex components; The shortcomings of its implementation are concentrated in the corrosion of refractory materials in the furnace body, HF off-gas scrubbing, precise monitoring of by-products, and control of fluorine mass balance. Fluorine ultimately exists in the form of terminal fluoride salts or washing derived mineral sinks. The existing core bottleneck lies in how to ensure the repeatability of heterogeneous waste mineralization processes and avoid underestimation and omission of gas-phase or refractory bound fluorine. The route of molten alkali mineralization has only been validated in pure fluoropolymer systems, and there is a lack of large-scale data on diluted composite products; The core implementation burden is the equipment corrosion, chemical control, washing salt load, and CaF_2 precipitation separation cost of high-temperature strong alkali system. Fluorine can form a stable terminal mineral sink represented by CaF_2, and the main bottleneck lies in the comprehensive cost evaluation of raw material dilution effect and reactor adaptability. The research evidence for the mild-reduction liquid-phase route comes almost entirely from simplified model substrates such as powders and films. Due to factors such as interface mass-transfer limitations, high reagent sensitivity, low processing flux, and poor tolerance to fillers and aging, a stable and reliable fluorine fate system has not yet been developed. The core unresolved problem is how to convert surface-selective reactions into bulk defluorination of real products. The sodium dispersion process can achieve near-quantitative NaF generation in pure PTFE solid systems, but validation data for heterogeneous products are very sparse. The shortcomings of its implementation are mainly in the safety control of pyrophoric sodium, ether solvent management, reaction kinetics, and the difficulty of solid-liquid separation, mixing sensitivity, and the presence of intermediate chemical sinks, primarily in the form of NaF. The core bottleneck is whether complex products can be safely disposed of without deep pre-crushing and purification.

Table 3. Real feed evidence, dominant deployment liabilities, and likely sink classes across representative PTFE management routes. The comparison is a cross-study qualitative synthesis, not a normalized head-to-head benchmark, because feed substrates, scales, and reporting boundaries differ across the cited sources [16,17,38–42,45,47,99,100].

Route	Evidence Basis beyond Neat Powder	Dominant Deployment Liabilities	Likely Sink Class	Most Serious Unresolved Question
High temperature destruction	Strongest real feed basis, including PTFE incineration and mixed fluoropolymer pilot studies [16,17]	Furnace integrity, hydrogen fluoride (HF) scrubbing, refractory attack, byproduct monitoring, full fluorine balance	Terminal fluoride salts or scrubber derived mineral sinks	Can heterogeneous waste be mineralized reproducibly without undercounted gaseous or refractory bound fluorine?
Molten hydroxide fluorine mineralization	Defined fluoropolymers, little evidence yet on dilute composite products [38]	Corrosion, caustic handling, wash water, salt load, CaF_2 precipitation and separation	Robust terminal mineral sink, potentially CaF_2	Can the chemistry remain credible once feed dilution and reactor compatibility are priced in?
Mild reductive solution routes	Powders, films, and compositionally simplified solids dominate [39,82–93,96]	Interfacial access, reagent sensitivity, low throughput, limited tolerance to fillers and ageing	Mechanistic proof of concept more than established sink	How can surface selective chemistry be translated into bulk conversion on real products?
Sodium dispersion	Strong data on PTFE solids, but sparse evidence on heterogeneous articles [40]	Pyrophoric sodium handling, ether solvent management, mixing sensitive kinetics, solids separation	Intermediate chemical sink, chiefly NaF	Can heterogeneous products be treated safely without extensive precomminution and purification?
Mechanochemical fluoride recovery or upcycling	Dry PTFE solids and limited article evidence, including thread seal tape [48–50]	Media wear, dust control, jar contamination, post milling salt and carbon conditioning	Intermediate or circular sink, depending on fluoride quality and downstream demand	Can reagent quality fluoride be delivered at volumes commensurate with diffuse PTFE waste?

Although the mechanochemical fluorine recovery and upgrading cycle route has shown near quantitative fluorine release and direct fluorine resource utilization potential in laboratory pure powder systems, from the perspective of real raw material validation in Table 3, it has only been validated on dry PTFE solids and a small number of simple products (such as threaded sealing tapes), and its adaptability to

mixed waste materials with uneven composition, filler content, and aging in industrial scenarios is significantly insufficient. Its deployment is simultaneously constrained by multiple engineering factors such as grinding medium wear, dust prevention and control, cross contamination of ball milling tanks, and post-treatment purification of fluoride salts and carbon phases in the products. Fluorine carriers belong to intermediate or cyclic fluorine sinks, and their actual value highly depends on the purity of recovered fluorine and the downstream demand scale. The core unresolved issue is whether it is possible to stably output reagent-grade fluorine sources at a scale that matches the volume of dispersed PTFE waste. Overall, the real-feed evidence summarized qualitatively in Table 3 indicates that, despite their high energy demand and substantial equipment and off-gas treatment costs, high-temperature processes remain the only mature route demonstrated for mixed industrial fluorine-containing waste. Emerging routes such as mechanochemistry offer milder conditions and greater potential for fluorine recovery, but they remain constrained by solid-state mass transfer and stringent feed-homogeneity requirements, leaving a substantial gap for the treatment of complex industrial waste streams.

7. Technoeconomic Constraints, Data Availability, and Cost Drivers

The previous text qualitatively described various PTFE disposal routes from the perspective of process performance. From the perspective of engineering implementation and industrialization promotion, the technical and economic constraints composed of infrastructure investment, energy consumption level, chemical consumption, and operation and maintenance costs are the core elements that determine the applicable scenarios and promotion potential of the process. Based on the core implementation shortcomings of various processes in Table 3, the cost composition and economic boundaries of the five routes can be systematically decomposed to address the insufficient discussion of cost dimensions in existing research. Table 4 maps the availability of technoeconomic and life-cycle evidence before route-level cost drivers are discussed.

Table 4. Availability of technoeconomic and life-cycle evidence. No route currently has a harmonized per-ton PTFE cost, energy, and carbon-footprint comparison under equivalent feed and boundary conditions. The entries below therefore separate reported evidence from inferred cost drivers.

Route	Evidence Status	Main Cost Drivers	Carbon-Footprint Evidence	Key Limitation
High-temperature destruction	Pilot and industrial operating evidence exists, but not usually normalized for PTFE-only feeds	Furnace operation, refractory corrosion, HF scrubbing, residue management	Route-specific LCA scarce; depends strongly on energy source and gas cleaning	Strongest feed tolerance, but normalized cost comparison remains absent
Molten hydroxide mineralization	Bench-scale or defined-feed evidence	Caustic consumption, corrosion-resistant reactor, washing, CaF_2 separation	Not reported on a harmonized basis	Limited evidence for mixed or filled products
Mild reductive solution routes	Laboratory proof-of-concept evidence	Stoichiometric metal/organometallic reagents, solvent handling, low throughput	Not reported	Bulk conversion and real-feed scope unresolved
Sodium dispersion	Strong PTFE-solid conversion data, limited heterogeneous-feed data	Pyrophoric sodium, THF recovery, mixing control, solids separation	Not reported	Safety and heterogeneous-product performance unresolved
Mechanochemistry	PFAS remediation scale-up evidence exists; PTFE upcycling remains mostly lab to decagram scale	Milling electricity, media wear, dust control, salt/carbon separation	Not normalized to PTFE waste	Potentially competitive, but scale and reagent-quality evidence remain incomplete

The high-temperature destruction route is currently the most industrialized disposal technology, and its economic advantage is first reflected in the lower marginal cost of infrastructure. Existing industrial hazardous waste incinerators can be adapted to dispose of fluorine-containing waste through moderate anti-corrosion measures and tail gas upgrading, without the need to build a new reaction system, and the scale effect is significant. But there are rigid cost expenditures on its operation and maintenance end: high-temperature HF flue gas will continue to corrode the refractory materials of the furnace body and the lining of the flue, requiring regular replacement of refractory bricks and anti-corrosion coatings, resulting in continuous equipment maintenance costs; At the same time, the tail gas washing unit needs to continuously consume calcium based and sodium based alkaline solutions to capture HF flue gas, and the consumption of chemicals and the disposal of hazardous waste from washing sludge constitute the core components of long-term operating costs. Normalized per-ton PTFE costs are not consistently reported, although high-temperature treatment remains the most mature option for heterogeneous feeds. Its strong feed tolerance offers an economic advantage for large-scale treatment of complex mixed industrial waste, consistent with the evidence summarized in Table 3.

The cost pressure of the molten hydroxide mineralization process is concentrated on both infrastructure investment and end-of-pipe solid waste disposal. Because the reaction must be carried out in a molten, strong-alkali environment at around 500 °C, the reactor material must have high-temperature resistance and strong corrosion resistance. Nickel-based special alloys or specialized anti-corrosion liners are typically used, and the infrastructure investment per reactor is significantly higher than that of conventional incineration systems. At the operational level, in addition to the significant stoichiometric consumption of NaOH, the reaction system will generate high-salinity wash wastewater and mixed salt residue, requiring additional wastewater treatment and hazardous waste disposal, resulting in a triple cost combination of reagent consumption, salt-residue disposal, and wastewater treatment. At the same time, this process requires high purity of raw materials, and composite filling waste requires pre-sorting and purification, further increasing the overall disposal cost. Therefore, this route is most plausibly applicable to high-purity sorted PTFE waste, and its economic feasibility decreases significantly for low-grade mixed waste, which fully corresponds to the shortcomings of prominent corrosion, high salt load, and limited range of raw material adaptation in Table 3.

Both mild liquid-phase reduction and sodium dispersion processes are reduction-defluorination routes under mild conditions, but both are limited by reagent costs and are difficult to scale up. The core cost bottleneck of mild liquid-phase reduction routes, represented by magnesium reagents, lies in the reaction reagents themselves: this type of functional metal-organic reagent is a fine chemical, with complex synthesis pathways, high procurement costs, and the reaction requiring large stoichiometric consumption. The cost per unit mass of PTFE is much higher than that of inorganic reaction systems. Due to the limitations of interface mass transfer, the single-batch processing capacity is extremely low, and the equipment capacity amortization cost is extremely high. At present, it remains a laboratory-stage PTFE route and lacks evidence for economies of scale. Although the sodium dispersion process can achieve near quantitative defluorination at room temperature with low direct thermal-energy demand, it also faces high reagent and safety operation and maintenance costs: metallic sodium is a flammable and explosive controlled hazardous chemical, and the safety protection costs in storage, transportation, and closed feeding processes are significant; The ether solvents such as tetrahydrofuran used in the reaction require a distillation recovery system, and the solvent purification loss and distillation energy consumption constitute the continuous operating cost. In addition, the additional investment in solid-liquid separation and the safe disposal of the reaction residue raise the overall disposal cost. Currently, it is suitable only for small-scale, high-value fluorine recovery scenarios.

The cost structure of the mechanochemical fluorine recovery and upgrading cycle route presents a distinct feature of "mid-term energy consumption and medium loss as the main factors, and potentially lower downstream wastewater and off-gas management burdens". The direct operating costs mainly stem from the continuous electricity consumption of the ball milling equipment, the regular wear and replacement of grinding media (zirconia balls, stainless steel balls) and ball milling tanks, and the need for supporting dust-prevention and closed-material collection systems. The core cost advantage of this route is that it does not require a high-temperature heating system or a large amount of organic solvents. The entire reaction process is carried out in the solid phase, and the amount of wastewater and exhaust gas generated is extremely small, greatly reducing the cost of final disposal of the three wastes. When combined with inexpensive inorganic additives such as potassium phosphate, it can completely replace high-priced metal reagents, further reducing reagent costs. Because normalized PTFE-specific mechanochemical cost and energy data remain scarce, this

route should be described as potentially cost-competitive rather than already economically superior. At present, however, laboratory-scale equipment amortization remains high, and separation and purification of fluoride salts and carbonaceous products have not been fully developed. Its short-term cost therefore cannot yet be compared reliably with mature high-temperature incineration.

Overall, the cost structure of the five types of PTFE disposal processes shows significant differentiation: high-temperature incineration, which is suitable for large-scale mixed waste at a moderate comprehensive cost, is currently the mainstream mature choice in the industrial setting. The route of molten alkali mineralization and liquid-phase reduction can only cover the subdivision scenarios of high-purity waste due to equipment and raw material cost limitations; Although the scale of the mechanochemical route is currently insufficient, it is a potentially cost-competitive direction if continuous milling, product separation, and feed pretreatment can be demonstrated at scale due to its potentially reduced wastewater and off-gas burdens, adaptability to inexpensive inorganic additives, and potential for fluorine resource utilization. The core path of low-cost improvement in the future lies in: based on mechanochemical processes, using cheap phosphate and calcium-based additives to replace high-cost alkali metal and organic metal reagents, while optimizing ball milling parameters, developing continuous equipment to reduce unit energy consumption, and improving raw material uniformity through simple pretreatment and sorting processes. While ensuring defluorination efficiency, it promotes the development of processes towards low cost, scale, and resource utilization.

8. Conclusions and Outlook

End of life PTFE management has entered a more exacting phase, in which the strongest recent studies no longer ask only whether PTFE can be attacked, but instead follow where fluorine and carbon travel, what it costs to direct them there, and whether the resulting endpoint is benign, recoverable, or synthetically useful. From this literature there emerges a coherent design logic. C-F bond cleavage must be coupled immediately to a robust fluoride sink, because routes that do so, whether through molten hydroxides, sodium dispersion, or mechanochemical phosphate or alkali systems, deliver more credible endpoints than routes that rely on bond scission alone [38–40,48–51,93]. PTFE accessibility is as important as reagent strength, since semicrystallinity, filler content, article architecture, and interfacial renewal determine whether a chemistry remains superficial or becomes truly bulk relevant [37,39,40,70–72,90–92,101]. Carbon fate must be treated as a coequal design variable, because defluorination that leaves carbon in volatile fluorocarbons, poorly defined residues, or weakly constrained gas streams cannot be regarded as a complete solution [16–23,48–50].

Read alongside Table 3, these design rules also show that deployment plausibility is not a polite concluding add on but the location where each route externalizes difficulty. Thermal routes displace difficulty into furnace integrity, byproduct suppression, and gas scrubbing. Molten hydroxides embed it in corrosion management and salt handling. Sodium dispersion exchanges thermal severity for reagent safety, solvent control, and solids separation. Mechanochemistry shifts the burden towards media wear, dust management, and the preservation of fluoride quality through a solids intensive workflow [16,17,38,40–42,45,47,99,100]. What often makes one route appear superior on paper is therefore little more than the choice of where the burdens are counted.

These route-specific burdens are synthesized in Figure 6, which is intended as a decision map for the review as a whole. The figure places high-temperature destruction, molten-hydroxide mineralization, mild reductive chemistry, sodium dispersion, and mechanochemical recovery on a common axis of feed tolerance, fluorine-sink quality, and deployment liability. Read together with the sink-quality grading in Table 2 and the evidence-availability map in Table 4, Figure 6 clarifies why route selection cannot be based on conversion yield alone. A high fluoride yield on neat PTFE powder may still have limited deployment value if feed heterogeneity, separation burden, reagent safety, or downstream fluoride demand remain unresolved.

Once that accounting is made explicit, it becomes difficult to sustain the fiction that pristine PTFE powders are an adequate benchmark for end-of-life chemistry. Fluoropolymers are often present only in small amounts within complex products, as coatings, seals, membranes, composites, or additives rather than neat polymer streams, and fluoropolymer specific life cycle analyses show that they sit uneasily within low carbon and circular economy ambitions despite their functional importance [3,4,11]. At the same time, recent overviews of fluoropolymer uses, PFAS alternatives, and polymer of low concern debates show why end of life strategies cannot be separated from broader questions of essentiality, substitutability, and regulatory framing [6,7,10]. For that reason, the more meaningful tests are expanded PTFE membranes,

filled gaskets, aged electrical components, mixed fluoropolymer fractions, and postconsumer articles carrying heterogeneous binders and contaminants, not merely the neat powders and simplified films that continue to dominate mechanistic proof of concept studies.

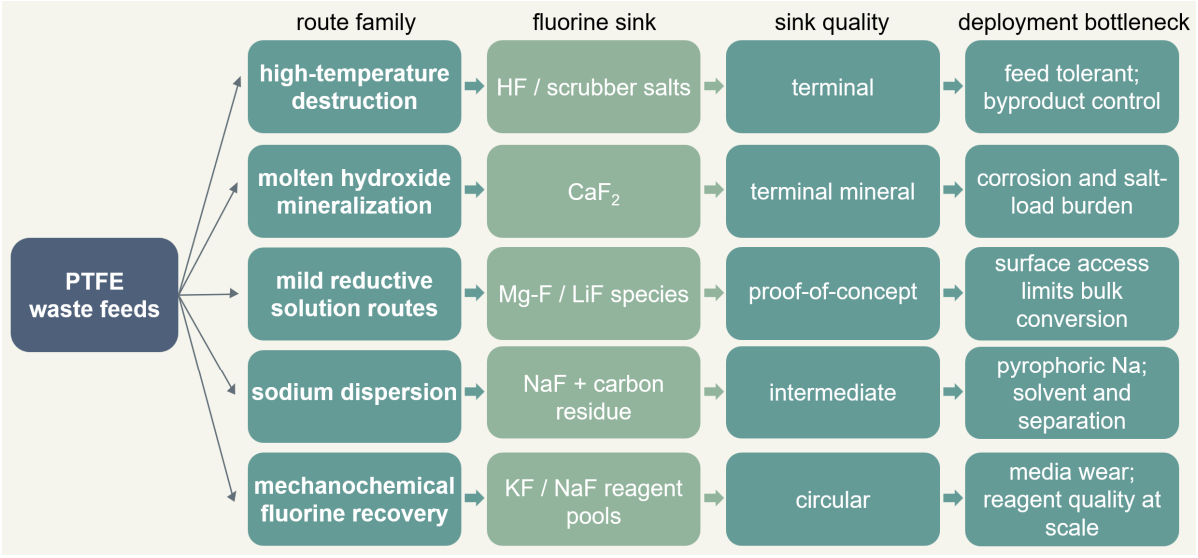

Figure 6. Integrated decision map for PTFE end-of-life chemistry. The author-drawn scheme links the major route families to their dominant fluorine sinks, functional sink-quality classes, feed-scope evidence, and scale-up bottlenecks. It connects the mechanistic endpoints discussed in Sections 3–6 with the deployment and cost constraints summarized in Tables 2–4.

The same literature also points away from the hope that a universal single-step solution is waiting just beyond the present state of the art, because across the wider PFAS treatment field fit-for-purpose process trains are increasingly favoured precisely on the grounds that no single technology is optimal for every matrix, concentration range, or fluorine inventory [56–58,60–64]. For PTFE-rich solids, that recognition may favour thermal elimination coupled to dedicated fluoride capture. For sorted fluoropolymer fractions, it may favour chemically or mechanochemically directed fluorine recovery. For dilute fluorinated burdens embedded in products, pretreatment and concentration steps will almost certainly be necessary. PTFE-specific recycling perspectives, broader plastic chemical-recycling analyses, and even industry-facing fluoropolymer recycling documents all converge on the same practical implication: sorting, hybrid processing, and endpoint-specific design are more realistic than any universal one-reactor solution [11–13,102]. Advanced reduction processes based on hydrated electrons (Figure 7a) [103] and recent photocatalytic electron-transfer routes for PFOS in water (Figure 7d) [96] show that, once electron delivery and product trapping are tightly coupled, even highly fluorinated targets can be pushed much closer to complete defluorination.

Broader PFAS degradation chemistry offers cross-system guidance for future PTFE treatment. Hydrated-electron reduction of PFCAs (Figure 7a) [103], persulfate activation (Figure 7b) [104], photo-oxidative chain shortening of PFOA (Figure 7c) [105], and photocatalytic electron transfer to PFOS (Figure 7d) [96] illustrate reductive and oxidative routes to C–F bond cleavage. Their direct translation to insoluble, semicrystalline PTFE remains unproven and would require continuous interfacial renewal together with immediate fluoride capture.

A correspondingly stringent reporting culture is now needed if destruction, fluorine mineralization, and upcycling are to be compared on genuinely common ground. At minimum, studies should report PTFE conversion, inorganic fluoride yield, closed fluorine mass balance, carbon speciation, volatile fluorinated products, reagent inventories, energy input, corrosive secondary streams, and the usability of any recovered fluoride [52–54,106]. Technoeconomic and life-cycle analysis should no longer be treated as optional add-ons, because recent reviews show that costs and climate impacts of PFAS treatment vary widely with concentration, matrix, and treatment train, while fluoropolymer life-cycle assessments underscore that end-of-life innovation, although necessary, is not sufficient on its own [3–5,57–64]. The most consequential conceptual shift, then, is from disposal to fluorine stewardship. PTFE should no longer be treated only as an exceptionally recalcitrant waste, but as a concentrated reservoir of fluorine whose end-of-life chemistry can be designed either for safe terminal capture or for reuse within a genuinely fluorine economy.

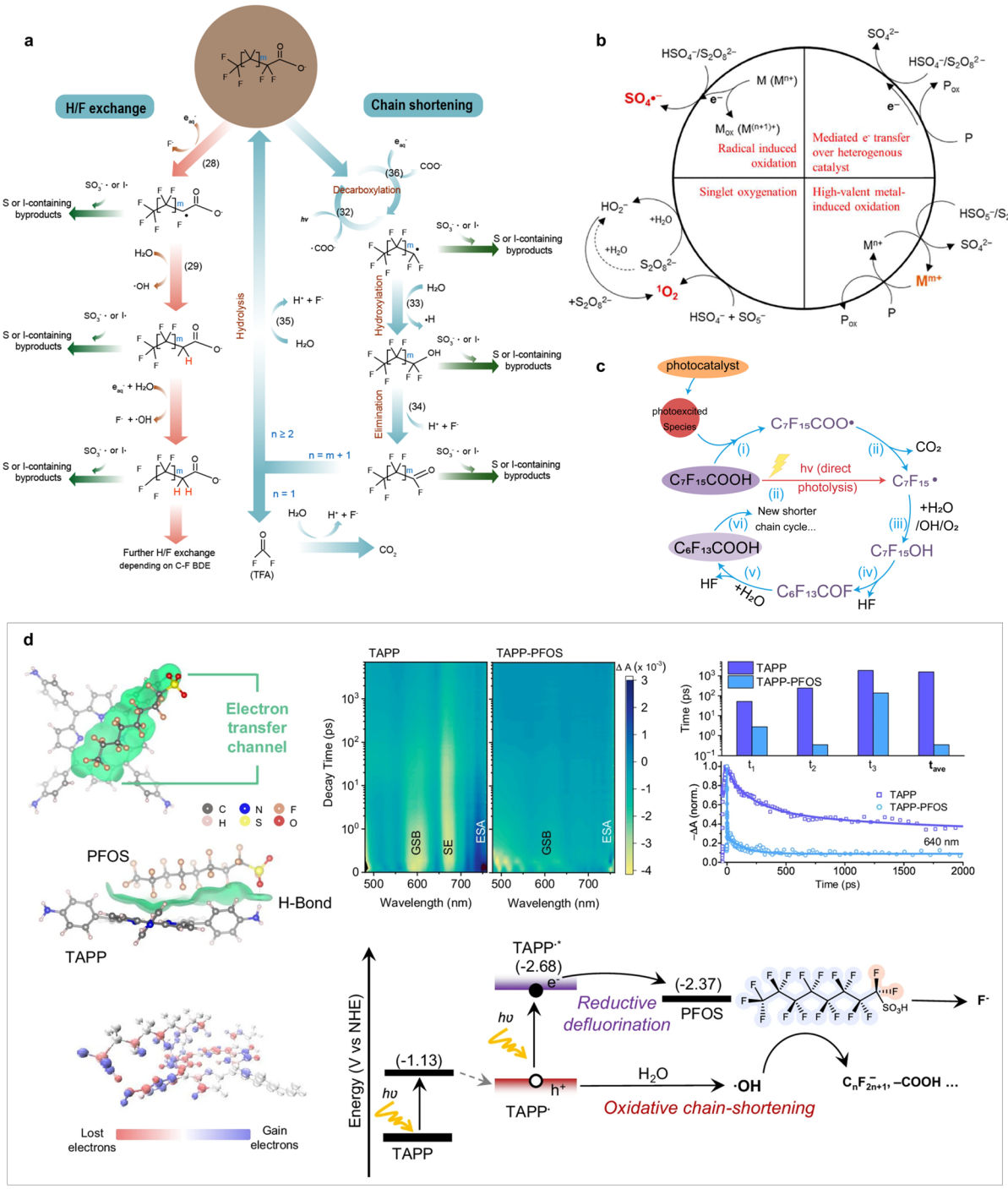

Figure 7. Broader PFAS defluorination chemistries that may inform future PTFE process design. (**a**) Major pathways in hydrated-electron reduction of perfluorocarboxylic acids (PFCAs). (**b**) Possible oxidative pathways induced by peroxymonosulfate (PMS)/peroxydisulfate (PDS) activation. (**c**) Common photo-oxidative degradation pathway for perfluorooctanoic acid (PFOA). (**d**) Photocatalytic electron-transfer and reductive defluorination of perfluorooctanesulfonic acid (PFOS) in water, adapted from Ref. [96] under the Creative Commons Attribution-NonCommercial-NoDerivatives 4.0 International License (https://creativecommons.org/licenses/by-nc-nd/4.0/).

Author Contributions

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Conflicts of Interest

The authors declare no conflict of interest.

Use of AI and AI-Assisted Technologies

No AI tools were utilized for this paper.

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