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Review

A review of hydrofluoric acid and its use in the car wash industry

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ABSTRACT

Hydrofluoric acid (HF) is a common ingredient in car wash cleaning solutions mainly because it is highly effective and relatively inexpensive. Particulate matter from brake pads and discs, tire wear, and abrasion of road surface accumulated on the exterior of automobiles are aggressively removed with the use of car wash cleaning solutions containing HF. The unique properties of HF to dissolve silica, concrete, most metals, and metallic oxides cause effective breakdown of rust, road dust, and grime on automobiles. However, HF is a very caustic and a highly toxic substance. Due to hazards associated with the storage, use, and exposure of HF to humans and the environment, there is a need to find safe, yet equally effective alternatives to HF as a cleaning agent. Improvements in cleaning processes, development of available technologies, and utilization of cleaning products containing natural and various benign polymers and surfactants are healthy and environmentally sound alternatives to HF for car wash applications. However, these alternatives may not be as effective as HF. Efforts geared towards finding a replacement for HF remain a challenge, but the outcome would render several benefits to the car wash industry, including abating pollution and providing a safer working environment for everyone.

Contents

1. Introduction

Hydrofluoric acid (HF) is a valued chemical in the academic, domestic, and industrial settings, being a precursor to numerous products and materials [1]. Large quantities of crude HF were first prepared by Carl Wilhelm Scheele in 1771 [2]. In the late 1800s and early 1900s, HF was utilized for glass etching, foundry scale removal, and sodium fluoride compound and high-octane fuel productions. The results of these applications have given birth to the use of HF as a primary ingredient in car wash cleaning solutions. Historically, most car wash cleaning products are based on detergents containing mild alkalis and dilute HF, formulated to loosen and eliminate dirt and grime on automobiles [3]. As the global automotive industry grew, there had also been activities

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involving the use of HF in professional car wash businesses, including those in car service and maintenance sector, due to the need for cheaper, more effective, industrial strength cleaning solutions. A clean automobile has become a necessity since then as more people washed their automobiles on a regular basis. Today, it is estimated that at least 50 car wash systems are installed annually by the United States and European manufacturers [4].

Since 1939, professional car wash businesses offer consumers an easy, time-saving, and practical way to wash dirt and grime from their automobiles [5,6]. Cleaning an automobile basically consists of the actual removal of oil and dirt, and then treatment to provide protection [7]. Degreasing solvents and cleaning agents remove traffic grime and particulate matter on automobiles, then the subsequent application of wax polishes and protects coatings. The operation of professional car wash facilities, both traditional and modern, generally falls under the following categories: hand car wash, self-service, in-bay automatics, tunnel washes, chemical car wash, and steam car wash facilities [8]. In the conveyor-operated car wash, the car moves by means of a conveyor through a tunnel and is washed by either friction or frictionless system. The frictionless system uses high-pressure nozzles to spray the car with cleaning solutions, whereas in the friction system, a series of brushes wash the car when moving through the system. In the in-bay automatic process, the car remains stationary while a machine moves back and forth as it washes over the vehicle. In self-service stations, the customer is responsible for washing the car using a low-pressure brush or hoses with nozzles that dispense either water or the cleaning solution at controllable amounts and pressures. In both conveyor and in-bay automatic systems, workers are needed to physically spray some chemicals on the car. The ideal car wash cleaning solution removes road dust, rust stain, dirt, films from brakes, and grime from the automobile with minimal effort. HF-based car wash cleaning solutions accomplish this task effortlessly.

Along with the popularity of HF comes the complexity of its regulatory laws due to its harmful effects to humans and the environment. Significant local and systemic toxicity may occur from HF by inhalation, oral, ocular, and dermal exposures during washing. Therefore, there have been strong efforts in the automotive industry to develop safer car wash cleaning solutions and to improve available car wash technologies [9]. As a result of this move, the number of professional car wash facilities that use HF has declined and car wash operators are required by law to reuse and pre-treat their effluent wastewater and maintain wastewater discharge permits [10]. In recent years, these facilities use water reclamation systems and energy usage reduction technologies. However, 44.5% of car owners in the U.S. alone (approximately equivalent to 61 million passenger cars in 2008 data [11]) still prefer driveway or backyard washing and at least 75% of all cars are washed at home at least once a year [10]. This is a concern since HF is still being used as an ingredient in a number of common commercial cleaning solutions. Categorized as an unregulated car wash facility, driveway washing also generates hazardous wastewater that ends up in the storm drain and could potentially contaminate ground and surface water. Hence, some state and local institutions have begun campaigns to encourage consumers to utilize regulated but costly professional car wash facilities as opposed to driveway and mobile charity car washing by hand.

To date, there are no academic institutions or public laboratories that directly focus their research on the fundamental chemistry of HF for car wash applications. This is not surprising not only because of the unusual and difficult nature of HF systems but also because almost all the extensive research and development of the alternatives to HF-based cleaning products are being done by chemists in industry for commercial use. However, this does not mean that there are no research facilities (both academic and industrial) capable of undertaking such a research effort.

In this literature review, we provide background information on the sources, global production, and several uses of HF. The physicochemical properties of HF, toxicity, harmful effects to humans and the environment, and regulations pertaining to its use, are also reviewed. We also highlight materials selection and storage guidelines for HF, car wash cleaning formulations, and sources and properties of non-exhaust particulate matter that accumulate on automobiles from road traffic. Primary attention is given to the use of HF in car wash cleaning applications including an explanation of its effectiveness against typical brake and road dusts. In the last section, recommendations and a summary of possible candidates for HF replacement that are found in domestic and industrial settings are given.

2. Sources of hydrofluoric acid

The mineral fluorite, commonly called as fluorspar (CaF_2), is the important starting material for the production of hydrogen fluoride, fluorine, and sodium fluoride [12]. Other alternative starting materials include fluorapatite ($Ca_5(PO_4)_3F$) and cryolite (Na_3AlF_6). Hydrogen fluoride, the most important manufactured compound of fluorine, is also generated upon combustion of many fluorine-containing compounds such as products containing Viton® and polytetrafluoroethylene (Teflon®) parts [13]. Fluorite is found as deposits in various parts of the world, notably in China, Germany, Austria, Switzerland, England, Norway, Mexico, Canada, and Kenya [14]. In the U.S., commercial mining for the production of fluorite was conducted in Illinois until 1995. As of today, the National Defense Stockpile is the source for all domestic U.S. supplies of fluorite. Small quantities of synthetic fluorite are also produced from industrial waste streams [15].

HF is produced from anhydrous hydrogen fluoride, a colourless gas or liquid at ambient temperature. HF is also a product of hydrolysis by moisture of fluorine-containing compounds such as carbonyl fluoride, BF_3, PF_5, SiF_4, SF_4, and PF_3 from volcanic emissions [16]. Ocean spray and dust from the weathering of fluoride-containing rocks and soils, and anthropogenic activities are the other sources of airborne fluoride compounds [17,18].

When anhydrous hydrogen fluoride is released into the atmosphere, contact with water vapour leads to immediate fuming and formation of a white mist [19]. Anhydrous hydrogen fluoride is normally manufactured at a purity level of 99–99.9%, whereas HF is primarily produced commercially as a 70% solution [20]. Electronic and reagent grades HF of 5–52% are also manufactured industrially [20]. Essentially all anhydrous hydrogen fluoride is manufactured worldwide by the chemical reaction of CaF_2 and H_2SO_4, owing to Gay Lussac and Thernard, the first chemists who managed to obtain pure form of HF in 1809 [21]. When combined in heated kilns at 538 K, CaF_2 and H_2SO_4 react to produce anhydrous gaseous hydrogen fluoride and solid $CaSO_4$ as shown in Equation 1 [22].

$$CaF_{2(s)} + H_2SO_{4(l)} \rightarrow 2HF_{(g)} + CaSO_{4(s)} \qquad (1)$$

This process utilizes acid-grade fluorite ($\geq$97.5% CaF_2), which is distilled with concentrated H_2SO_4. Hydrogen fluoride leaving the reactor is purified by distillation after being condensed. HF is then rapidly obtained by dissolving the anhydrous hydrogen fluoride in water.

Hydrogen fluoride is also produced as a by-product of the extraction of the fertilizer precursor H_3PO_4, which is obtained from the mineral apatite ($Ca_5(PO_4)_3(F,Cl,OH)$) [13]. Acid digestion of fluoroapatite in apatite sources releases a gaseous stream consisting of hydrogen fluoride, SO_2, H_2O, and particulate matter.

The gaseous products are separated from the solids and treated with H_2SO_4 and oleum to yield anhydrous hydrogen fluoride. The production of HF is accompanied by the dissolution of silicate minerals which produces significant quantities of fluorosilicic acid (H_2SiF_6) [13].

3. Global production and the United States imports of hydrofluoric acid

In 1931, HF was first commercially produced and its production has steadily increased reaching 161,260 and 375,000 metric tons in years 1967 and 1974, respectively [23]. In the 2008 data, China, Mexico, Mongolia, and South Africa registered the highest quantities of acid and metallurgical-grade fluorite produced with 3,250,000, 1,058,000, 380,000, and 316,000 metric tons, respectively [24]. Also in 2008, HF and aluminium fluoride production is the largest end use or product of consumption of fluorite (containing >97% CaF_2) in the U.S.

Table 1 presents the largest producers of commercial HF in North America [25], whereas Table 2 shows the U.S. imports of HF for years 2008 and 2009 [15]. Honeywell continues to be the largest producer of HF in the world. Honeywell is particularly proactive in providing safety information on the proper handling and transportation of HF [26]. E.J. du Pont de Nemours & Co. Inc. (DuPont) ceased merchant sales of anhydrous HF in 2002 [25] but continues its production for captive use at the DuPont facility in La Porte, Texas. The majority of the U.S. consumption of HF is supplied by imports. The U.S. imports of HF from 2007 to 2008 and from 2008 to 2009 decreased by 12.5% and 14%, respectively [24].

4. Uses of hydrofluoric acid

The practical value of HF for both industrial and domestic applications arises from its aggressive behaviour [27]. For example, HF is extensively used in the cleaning of stainless steel (a process called pickling) [28], etching glass, removing oxides from metals, exotic extraction of metals, and purification of quartz [29]. Manufacturers market large quantities of HF as drummed or packaged products. Fig. 1 illustrates the proportions of the major uses of hydrogen fluoride compounds [25]. Production of refrigerants including fluorocarbons such as hydrofluorocarbons, hydrofluorochlorocarbons, and fluoropolymers accounts for 60% of anhydrous hydrogen fluoride use [30]. Other uses include: chemical derivatives (organic and inorganic compounds having highly specialized and valuable properties, e.g., fabric or fibre treating agents, BF_3, SF_6 and F^- salts), 18%; aluminium manufacturing, 6%; stainless steel pickling, 5%; petroleum alkylation catalysts, 4%; uranium chemicals production, 3%; and miscellaneous uses (other markets), 4% [30,31]. Other compounds prepared from hydrogen fluoride are inorganic fluoride compounds of industrial importance including cryolite, Na_3AlF_6, and AlF_3. Inorganic fluorides including NaF and UF_6 are also prepared to produce HF.

Table 1
Largest producers of commercial anhydrous and aqueous HF in North America [25].

Producer	Production capacity (thousand metric tons/year)	Location
Honeywell	182	Geismar, Louisiana (U.S.) and Amherstburg, Ontario (Canada)
Quimica Flour	94	Matamoros (Mexico)
DuPont	80	La Porte, Texas (U.S.)
Solvay Fluor Mexico	36	Juarez (Mexico)
Alcan Aluminum	34	Jonquiere, Quebec (Canada)
Industrias Quimicas	7	San Luis Potosi (Mexico)
Quimobasicos	6	Monterrey (Mexico)
Total	439	

Table 2
United States imports for consumption of HF by country for 2008 and 2009 [15].

Country	2008	2009
	Quantity (metric tons)	Quantity (metric tons)
Canada	23,900	11,000
China	1,690	4,110
France	<0.5	0
Germany	562	404
India	71	120
Japan	1,240	559
Liechtenstein	1	0
Lithuania	0	<0.5
Mexico	105,000	97,600
Singapore	79	64
South Africa	0	13
Spain	0	<0.5
Switzerland	0	<0.5
Taiwan	34	49
United Kingdom	<0.5	<0.5
Total	~133,000	~114,000

The miscellaneous category includes applications such as glass etching or processing (quartz purification), herbicides, removing oxide impurities from metals and purification of rare metals (mining and drilling operations), semiconductor and electronics industry [32,33], fluorescent light bulbs, and cleaning solutions. The latter is an integral part of automotive industry [29] and the subject of this review.

The ability of HF to remove oxides from metals is the primary reason for its use in industrial and household rust and stain removers and car wash cleaning solutions [3]. Car washing is one of the most chemically intensive activities and car wash facilities continue to use HF in their daily wash routine due to its relatively inexpensive cost especially when purchased in bulk (i.e. 10–12% HF solution and other ingredients to be diluted in water in a 55-gal drum is the standard for fleet operations). On the average, the cost is $5 (U.S. dollar) cheaper than other cleaning agents or between $3 and $5/gal in an 8% diluted concentration [34]. A 1:30 HF to water dilution ratio is recommended by soap companies [34] but this ratio generally varies depending on the temperature and type of water to be used and the preferred strength of formulation.

Related to the use of HF as a car wash cleaning ingredient is its use in acid digestion in combination with other inorganic acids. Acid digestion is a common procedure being conducted prior to trace element analyses in environmental samples [35]. For example, solid samples have similar properties or compositions to those normally found in particulate matter that accumulates on automobiles. A study was conducted on sewage sludge samples and the total concentrations of Cd, Cr, Cu, Fe, Ni, Pb, and Zn in the samples were determined by digestion with the use of HF combined with HNO_3 and $HClO_4$, and aqua regia [36]. Another study determined Hg concentrations in walleyes using mixed

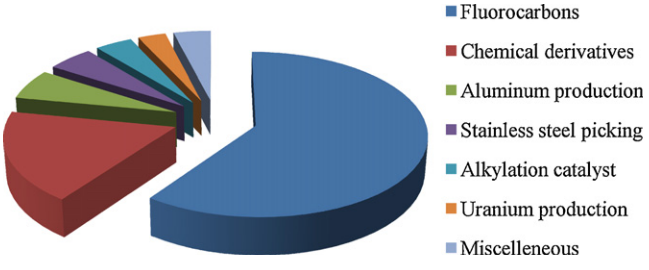

Fig. 1. Major uses of hydrogen fluoride compounds [25].

HNO_3 and H_2SO_4 digestion followed by cold vapour atomic absorption spectrometry, and mixed HNO_3 and HF digestion followed by inductively coupled plasma mass spectrometry [37]. The application of microwave digestion system for the safe and rapid digestion of dust samples using HF was also evaluated [38]. Deposited dust collected and reference samples representing municipal waste incineration ash, urban particulate matter, and river sediments were used as samples. Digestion of dust samples allowed recovery of Pb and Cd at over 80% with HNO_3 or aqua regia, and over 90% with a HF–HNO_3 mixture. HF was also used for digestion of geological samples containing radioactive elements. Following digestion of samples with HF, Hf was eluted along with Pt group elements [39]. This effect was attributed to a portion of the Hf forming stable fluorocomplexes that have distribution coefficients near zero on cation-exchange resins.

HF has been used in methods development for the extraction of carbonaceous particles [40]. A previous study involved two chemical treatments of biosolids and soil samples in an attempt to isolate the inorganic and organic components in these samples [41]. HF treatment was employed to remove mineral components and to isolate the biosolids and soil organic matter. HF treatment removed 56–82% of the biosolids mass and 93–95% of soil mass. Carbon contents of the HF-treated residues were in most cases well below what would be expected in pure organic matter (40–60%), indicating that not all inorganic species were removed. Results showed that the majority of carbon was recovered on HF treatment of biosolids (85–103%) and soil samples (67–74%).

Grass and deposition analyses after HNO_3 digestion and subsequent digestion with HF were conducted on samples from three different locations [42]. The main objective of the study was to test whether additional digestion with HF is an effective method to enhance detection of Sb in standardized grass. Sb enrichment near traffic was confirmed by monitoring with standardized grass cultures and total depositions. Compared to digestion using 70% HNO_3, grass analysis after digestion with 40% HF yielded double Sb concentrations in heavy traffic, in the rear and very low traffic, and in unwashed and washed grass locations.

A previous study demonstrated successful chemical formulations that exhibited Cu and W compatibility, and interlayer dielectric cleaning and selective Ti etching capabilities [43]. HF was used along with a Si precursor to protect SiO_2. The presence of H_2O_2 in the cleaning solution led to more than an order of magnitude suppression of Cu dissolution rates. This phenomenon was ascribed to the formation of interfacial CuO which dissolved at a slower rate in dilute HF. The kinetics of the reaction was determined to be first order with respect to both HF and oxygen concentrations. The formulation selectively stripped Ti film and removed post plasma etch polymer or residue while suppressing the etching rate of W, Cu, SiO_2, SiC, Si_3N_2, and C-doped SiO_2.

Due to the ability of HF to dissolve Fe oxides and silica-based contaminants, HF is used in pre-commissioning boilers that produce high-pressure steam [44]. HF is also useful for dissolving powdered rock samples prior to analysis since dissolution of some oxides including Ta_2O_5 and ternary oxides readily occurs. In a similar manner, HF is used to extract organic fossils from silicate rocks [45]. Fossiliferous rock may be immersed directly into the acid, or a cellulose nitrate film may be applied (dissolved in amyl acetate), which adheres to the organic component and allows the rock to be dissolved. Diluted HF (1–3% w/w) is used in the petroleum industry in combination with organic acid or HCl to stimulate the production of water, oil, and gas wells that contain sandstones [46].

5. Chemistry of hydrofluoric acid

To better realize how HF works in cleaning (i.e. removal of brake and road grime and dust) and to provide possible alternatives, it is helpful to have a comprehensive understanding of the physicochemical properties of HF. Table 3 summarizes some important physical properties of 70% HF [47–50].

Table 3
Some important physical properties of 70% HF [47–50].

Property	Value
Boiling point at 101.3 kPa	66.4 °C [47]
Freezing point	−69 °C [48]
Density at 0 °C	1.256 g/mL [49]
Vapour pressure at 25 °C	20 kPa [50]
Viscosity at 25 °C	0.61 mPa s
Specific heat at 25 °C	0.675 J/g °C

Dilute HF is classified as a weak acid and ionizes in aqueous solution (Equation 2) in a similar fashion to other common acids [22].

$$HF_{(aq)} + H_2O_{(l)} \leftrightarrow H_3O^{+}{}_{(aq)} + F^{-}{}_{(aq)} \tag{2}$$

Among the hydrohalic acids, only HF is not considered a strong acid as it does not fully dissociate in aqueous solutions and can dimerize (dimmers can lose one proton). The acidity of HF increases dramatically when its concentration approaches 100% due to high concentrations of bifluoride anion (HF_2^-, stabilized by a strong H–F hydrogen bond) that formed from the autoprotolysis of HF, as shown in Equation (3) [22]:

$$3HF \leftrightarrow H_2F^{+} + HF_2^{-} \tag{3}$$

HF has an acid dissociation constant of 6.7×10^{-4} (pK_a 3.17) in dilute aqueous solution at 298 K [51], corresponding to approximately 8% dissociation in 0.1 M HF solution. The azeotrope having 38% (w/w) HF and 62% (w/w) H_2O boils at 385 K. The known hydrates of HF such as $4HF{\cdot}H_2O$ (m.p. 261.6 K), $2HF{\cdot}H_2O$ (m.p. 197.5 K), and $HF{\cdot}H_2O$ (m.p. 237.5 K) can be isolated from 0.1 M HF solution [52]. However, dilute HF solutions have several unique physical properties; for example, they are 1000× less dissociated than HCl. The ionic dissociation equilibrium constants are 10–13 orders of magnitude smaller than those of other dilute aqueous solutions of halogen halides (HCl, HBr, and HI) [53].

The exact reason why HF behaves as a weak acid has been a subject of long debates [54–56]. Theoretical studies have provided detailed structural and dynamical descriptions of the elementary chemical events when HF dissolves in water [57]. These recent studies do not support the previous hypotheses that HF dissociates in water to form a very stable $F^{-}{\cdot}H_3O^{+}$ contact ion-pair complex instead of free ions formed by the ionic dissociation of the other members of the halogen halide series [52]. The incomplete dissociation of dilute HF in water is believed to be partly attributed by the high energy requirement to break the strong H–F bond. The thermodynamic cycle for the dissociation of HF in water suggests that the physical origin for dilute HF solutions to be weak acids has a large negative entropic contribution [52]. The HF ionic dissociation free energy, which is much greater than that for the other members of the halogen halide series (at 298 K, $T\Delta S^{0}{}_{r} = -31$, -17, -10, and -2 kJ/mol for HF, HCl, HBr, and HI, respectively) plays a significant role in the reaction equilibrium [52]. This property is mainly due to the large and positive hydration entropy resulting from the structure-making character of F^- hydrated in water [52].

The acidity of HF has been found to increase with its concentration [22,57] and is larger in H_2O than in D_2O ($K_a(H_2O)/K_a(D_2O) = 2$ at 298 K) [58]. Surprisingly, HF exhibits extensive ionic dissociation in amorphous solid water at very low temperatures (40 K) [52]. HF becomes a relatively stronger acid in ice than other weak acids with smaller pK_a values (stronger acids in liquid than

HF) presumably due to decreasing entropic contributions to the free energy. These findings are in agreement with the common knowledge that it is preferred to dope ice with HF by introducing extrinsic defects to enhance its electrical conductivity. The pK_a value of HF in ice was estimated to be very similar to its value in water [59].

HF attacks glass by reaction with SiO_2 to form silicon fluorides. This dissolution process proceeds as depicted in Equations (4) and (5) [60].

$$4HF_{(aq)} + SiO_{2(s)} \rightarrow SiF_{4(g)} + 2H_2O_{(l)} \quad (4)$$

$$6HF_{(aq)} + SiO_{2(s)} \rightarrow H_2SiF_{6(aq)} + 2H_2O_{(l)} \quad (5)$$

A previous study has found that the HF species are adsorbed at the Si lattice bonds. This adsorption weakens the Si–O bond in glass and brings about dissolution. The etch rate was found to be linearly dependent on the concentration of HF_2^- at low pH range [61]. Thus, the use of either stronger acids such as HCl, HNO_3, and H_2SO_4 or NH_4F in HF solutions to enhance etching for large area surface microstructures received considerable attention due to the catalytic role of H_3O^+ or NH_4^+ in the dissolution process [32,60].

Some reactions of HF with metal oxides are shown in Eqs. (6)–(9) [22,62].

$$6HF_{(aq)} + Al_2O_{3(s)} \rightarrow 2AlF_{3(aq)} + 3H_2O_{(l)} \quad (6)$$

$$4HF_{(aq)} + TiO_{2(s)} \rightarrow TiF_{4(aq)} + 2H_2O_{(l)} \quad (7)$$

$$6HF_{(aq)} + Cr_2O_{3(s)} \rightarrow 2CrF_{2(aq)} + F_{2(g)} + 3H_2O_{(l)} \quad (8)$$

$$4HF_{(aq)} + UO_{2(s)} \rightarrow UF_{4(aq)} + 2H_2O_{(l)} \quad (9)$$

Additionally, some reactions of HF with Al and Ti are shown in Equations (10) and (11) [63]:

$$6HF_{(aq)} + 2Al_{(s)} \rightarrow 2AlF_{3(aq)} + 3H_{2(g)} \quad (10)$$

$$8HF_{(aq)} + 2Ti_{(s)} \rightarrow 2TiF_{4(aq)} + 4H_{2(g)} \quad (11)$$

6. Material selection and storage guidelines, and car wash cleaning formulations

A notable disadvantage of the use of HF, however, is that it is impossible to do reactions with quartz or glass containers. High-silicon cast irons, stoneware, and glass are aggressively attacked by HF although the chemical reaction can be controlled [64]. The use of plastic vessels is one of the only ways for storing HF. Plastics such as polyethylene, polypropylene, polyvinylidene fluoride, and carbon-filled phenolics are resistant to up to about 70% HF concentration [64]. Polyvinyl chloride, elastomers (rubbers), and Pb show good resistance to HF at concentration limited to about 50–70%. Mg and its alloys resist corrosion attack by HF at concentration ≥5% due to surface passivation that occurs as a result of the formation of an insoluble MgF_2 film [64,65]. Plain C steels have higher corrosion resistance (64–100% HF) than low-alloy steels at ambient temperature. Perhaps the best containers used today for reactions involving HF are made of a Monel® material, an alloy primarily composed of Ni and Cu [66]. The Ni-31.5Cu-1.2Fe and 70Cu-30Ni alloys possess excellent resistance to HF at any concentration and up to temperatures of about 393 K and 338 K, respectively [64]. However, oxidizing molten salts have a propensity to increase the corrosion of these alloys. Copper–nickel alloys are also generally more expensive than stainless steels. Pb exhibits a fairly good resistance to HF in concentrations below 60% at ambient temperature. Precious metals such as Ag, Au, and Pt are not attacked by HF but they are far more expensive than Cu–Ni alloys.

HF should be stored in a cool, dry, ventilated, and shaded area. The storage area needs to have a coloured curb or barrier high enough to contain spills, along with a high flow wash area for those who come in contact with HF. The floor of the storage area is recommended to be acid-resistant and non-porous. Containers for HF solutions should not be stored for >3 months and must be inspected periodically for leaks.

Commercially available formulations in car wash cleaning solutions can be broadly divided into three major groups: detergent formulations, alkaline hard cleaners, and acid cleaners [67]. Detergent formulations have been commercialized for usage but not all of them are effective. Cars still require to be physically scrubbed to remove particulate matter adhered on the wheel surfaces. Alkaline hard surface cleaners consist of detergents, water-soluble organic solvents such as glycol ether, and alkaline materials such as NaOH, KOH, and/or alkaline silicates and phosphates [67]. Alkaline hard surface cleaners are also partially effective in removing wheel soils. The highly alkaline nature of such hard surface cleaners can damage rubber, glass, and painted Al surfaces [68]. Thorough rinsing is required; otherwise, alkaline cleaners tend to leave insoluble residues. Acid cleaners consisting of strong acids (HCl and H_2SO_4), weak and organic acids (HF, H_3PO_4, $H_2C_2O_4$, $HC_2H_3O_2$, glycolic, or citric acids), combinations of these acids, and compatible surfactants have been developed and commercialized. Acid cleaner formulations with HF are very effective in removing grime and road soils. In fact, HF-based acid cleaners are often used as wheel brighteners and pre-soak solutions. Acid cleaners have a disadvantage of being highly corrosive and hazardous. Most car wash cleaning solutions contain HF to clean motor vehicles due to the need of strong chemical cleaning [69]. However, HF can attack both protective wax coatings on a car and paint if not thoroughly rinsed. Concentrated HF reacts through the clear-coat finish and into the metallic wheel, which can cause premature oxidation resulting to pitted and dull chrome wheels.

7. Compositions and properties of brake pads/linings and the particulate matter that accumulate on automobiles

To better understand how HF is able to remove brake and road films, it is also important to identify the chemical compositions and properties of the particulate matter that make up these films. There are three major sources of particulate matter: wear of brake pads and discs, wear of tire, and abrasion of road surfaces [70]. While the latter two are present on the exterior of automobile prior to washing, it is the dust from brake pads and discs that contributes the greatest difficulty in the cleaning process. Traditional car cleaning products cannot remove this dust easily; hence, the reason HF is used. While brake discs are predominantly composed of Fe and are similar on most automobiles, there are essentially three major types of brake linings currently being used in the automotive industry as summarized in Table 4 [71].

Due to the small size of brake dust particles (typically <2.5 μm), surface passivation will not take place in the breakdown of such particles by dilute HF solutions [64]. Dirt could be washed with simple soap and water or all-purpose cleaner if the automobiles only had normal dirt on them. Thus, the type of particulate matter that gets on the automobile that need to be

Table 4
Classification of brake linings [71].

Classification	Compositions
Metallic	Predominantly metallic, steel fibres, copper fibres
Semi-metallic	Mixture of organic and metallic (30–65%)
Non-asbestos organic	Largely organic, mineral fibres, graphite

cleaned necessitates the use of an acid or a harsh cleaner. The brake pads, brake linings, and brake rotor themselves may cause such problems.

Brake pads have gone from polymeric to semi-metallic composition, which generally refers to the presence of Fe and steel in the formulation [72]. Semi-metallic brake pads are composed of fine powders of graphite, Fe or Cu, and small amounts of inorganic fillers and friction modifiers [72]. This helps bring the automobile to a quicker stop as well as prolongs the life of the pad. There are also other organic compounds in brake pad compositions and adhesive systems. Organic formulations often contain polymers such as Kevlar®, resins, and sometimes asbestos fibres [73]. However, manufacturers generally shifted towards producing non-asbestos organic formulations for safety reasons. Both organic and semi-metallic materials may contain Cu, although specific amounts depend on the manufacturer [74]. The debris of the shavings of the pads and the little bits of the brake rotors come onto the wheel, which results in deposits that stick on the breaking system and re-bind to the wheel. Less corrosion of the surrounding metal components occurs in ceramic brake pads because they have relatively low metal content. HF basically attacks a surface and dissolves the particulate matter on the surface. The more particulate matter that gets on the wheel, the deeper such particles embed themselves into the wheel and the more difficult the removal becomes. The accumulated brake dusts cannot be fully removed with water, compressed air, and ordinary cleaner. HF is very effective in dissolving some metals, an essential constituent of brake dust, and in breaking down adhesives. The effectiveness of HF is thus far much better than any other ordinary cleaning solutions.

At one point asbestos was a serious issue in the composition of brake dusts [75] but in 1986, the U.S. EPA placed a ban on the use of asbestos in brakes. The U.S. EPA required that new transportation vehicles have asbestos-free brakes by September 1993 [76]. As a result, all types of brake linings are now comprised of five major components: fibres (provide mechanical strength); abrasives (increase friction and maintain clean contact surfaces); lubricants (stabilize frictional properties); fillers (improve manufacturability and reduce cost); and binders (maintain structural integrity and thermal stability) [77]. Table 5 summarizes the materials commonly utilized for each of these components [77].

The current understanding of the physical properties and chemical compositions of brake lining materials and particulate matter generated as a result of brake wear is far from comprehensive. The complex nature and number of brake lining materials currently being used in automobiles, and the variety of factors that influence brake wear hindered extensive investigation of their physical properties. Research to date in the chemical analysis of brake dusts is actually limited. The literature lacks a thorough study of the characteristics of brake wear debris, according to Mosleh and Khemet [76]. Thorpe and Harrison further added that the exact composition of brake materials is considered proprietary by manufacturers and is therefore rarely fully disclosed [70]. All of the studies found in the literature were focussed on the elemental analysis of the chemical components of brake dusts as opposed to the identification of the actual chemical compounds themselves. The preferred analytical methods used for such analyses were inductively coupled plasma mass spectrometry and X-ray, both of which only provide information on the elements present in the samples. For instance, some of the samples examined provided the presence of the following elements:

Table 5
Typical components of brake linings [77].

Component	Percentage	Material
Fibres	6–35%	Various metals, carbon, glass, polymers (Kevlar®), and ceramics
Abrasives	Up to 10%	Alumina, iron oxide, silica, and zircon
Lubricants	5–29%	Graphite, metal sulfides/oxides, silicates, brass, bronze, and copper
Fillers	15–70%	Barite ($BaSO_4$), calcite ($CaCO_3$), mica (silicate mineral), vermiculite, cashew dust, and rubber particles
Binders	20–40%	Phenolic resins

- "Tire dust is a significant pollutant, especially as a source of Zn in the urban environment." [78].
- "Brake dust has been recognized as a significant pollutant for Cu, Sb, and Ba in the aerosols composition, and it contributed 47% of the total loading for Cu in urban runoff." [78].
- Road/tire sources include Al, Si, K, Ca, Ti, Mn, Fe, Zn and Sr [79].
- Brake sources include Cr, Fe, Cu, Zn, Zr, Mo, Sn, Sb, Ba and Pb [79].
- "Traffic appears to be responsible for the high levels of Ba, Cu, Cr, Mo, Pb, Sb, and Zn." [80].
- "...that the yellow road line markings were sources of Cr and Pb in heavy traffic road dust and that materials containing Fe as a major component, such as stainless steel were additional sources of Cr in both road dust and soakaway sediment." [81].
- Cars and trucks accumulate traffic soil and dirt composed of "sand, clay, Ca, Mg, Fe salts, C black, soot from exhaust emission, and rubber particulates from tires." [68].

Analysis of particle sizes ranged from about 0.35–2.5 μm [76,82]. These small particle sizes make them particularly susceptible to chemical attack from HF. Results from two research papers by Thorpe and Harrison and von Uexküll et al. provided elemental concentrations of three brake dust samples, presented in Fig. 2 [70,83]. The information suggests that elemental compositions are highly dependent on the type of brake pad being used.

Significant concentrations of Sb, a potential human carcinogen, have been quantified in brake pads and dusts in previous studies [84,85]. A recent study showed that SbS_3 is oxidized to SbO_3 in the braking process [83]. This indication of an oxidation of brake dust particles taking place during the braking process implies that the majority of chemical compounds are metallic or semi-metallic oxides of the elements, as depicted in Fig. 2. This hypothesis is supported by the fact that HF is very aggressive towards decomposition of brake dusts, whereas other stronger acids are much less effective.

Twenty-six metals have been determined in street dust sampled from five major cities around the world including

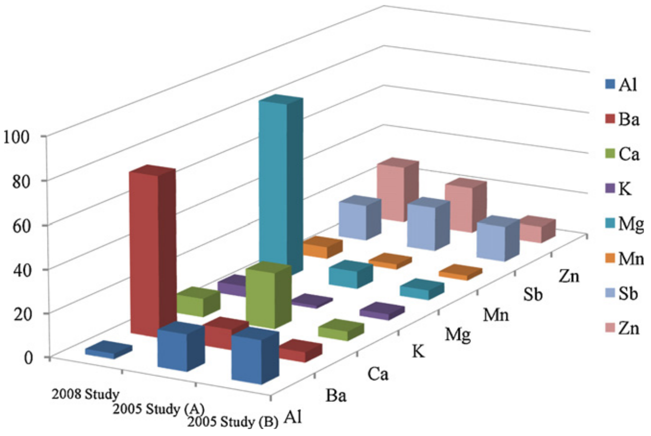

Fig. 2. Elemental concentration (g/kg) of various brake dust in 2005 and 2008 studies [70,83].

London (United Kingdom), New York (U.S.), Halifax (Canada), Christchurch (New Zealand), and Kingston (Jamaica) [86]. The metals were categorized into two groups: those that originate mainly from soil (Al, K, Na, Th, Ce, La, Sm and Ti) and those that originate primarily from other sources (Ca, Cd, Pb, Cr, Zn, Cu and Au) such as cement, tire wear, car emissions, and salt. The first group of metals was in lower concentration in London and New York than in the other cities, whereas the reverse holds for the second group of elements. The concentrations of most metals increased with corresponding reduction in size of the dust particles. In a separate study, Weckwerth found that aerosol component in ambient air in Cologne (Germany) contained Zn, Mo, Cu, Sb, Pt, and As as emission from various parts of automobiles [87].

A total of 96 street dusts and 96 roadside soils samples were collected from three different localities (urban, industrial, and peripheral) of the city of Kavala (Greece) and analyzed for Pb, Cu, Zn, Ni, Cr, Cd, As, and Hg contents [88]. Results showed that dust and soil samples from urban and industrial areas contained significant levels of the metals studied compared to the values obtained from the control site. Street dust distribution patterns were almost similar to those found for roadside soils. The results further indicated that urban and industrial street dust samples contain high levels of Pb, Cu, Zn, As, Cd, and Hg whose primary contributors were vehicular local traffic and the nearby phosphoric fertilizer and petrochemical industrial plants.

8. Effects of hydrofluoric acid exposure in humans and regulations relating to exposure

There are a number of research articles and case studies that review the adverse effects of HF in humans. The caustic and corrosive nature of HF, coupled with its chemistry, comes to play upon exposure [89]. Due to low dissociation constant of HF, it penetrates tissue more quickly than typical inorganic acids [90]. As a result, poisoning can readily occur through exposure of skin or eyes, or when inhaled or swallowed [91]. Inhaling the HF vapours (odour threshold is 0.042 mg/L) can cause ulcerative tracheobronchitis, hemorrhagic pulmonary oedema, hypocalcaemia (lack of enough calcium), hypomagnesaemia (lack of enough magnesium) [91,92]. The lowest lethal limit for a 5-min exposure to HF is estimated between 50 and 250 mg/L [93]. Depending on the concentration of HF, symptoms of such exposure may not be immediately evident as it gradually interferes with nerve function. Delayed treatment increases the extent and seriousness of the injury [94].

At present, it is still uncertain which ionized species of HF (F^-, H_2F^+, or HF_2^-) is the most dangerous to humans as the literature lacks a thorough study of the comparative toxicity of F^-, H_2F^+, and HF_2^-. This is likely due to the difficult nature of studying the chemistry of HF. However, the combined damaging effects of H^+ and F^- in the human body are well documented. For example, HF causes tissue damage by two different mechanisms [95]. Upon exposure, concentrated HF (high H^+ concentration) will immediately lead to corrosive burns similar to those caused by burns from strong acids. Secondly, the F^- being very lipophilic will penetrate the outermost layer of the epidermis and deep into the inner tissues [95] leading to painful necrosis, a characteristic of focal bacterial or fungal infections (liquefactive necrosis) [96,97]. The H^+ then separates from the F^- and attaches itself onto the enzymes that balance the pH which stabilizes tissues [94]. The H^+ damages the exterior surface of the cells in the body, whereas F^- destroys the interior cell. Fluoride ions bind with biologically important Ca^{2+} and Mg^{2+} in the body (Equations (12) and (13)), destroying cell membranes and nerves on their way to the bone [94,97,98]. Due to nerve damage, numbness renders the injured person unaware for several hours during

$$Ca^{2+}{}_{(aq)} + 2F^-{}_{(aq)} \rightarrow CaF_{2(s)} \tag{12}$$

$$Mg^{2+}{}_{(aq)} + 2F^-{}_{(aq)} \rightarrow MgF_{2(s)} \tag{13}$$

which the HF is diffusing throughout the body. Fluoride ions readily penetrate the skin causing deep tissue damage and decalcify the bone [94,99]. The reaction of F^- with Ca^{2+} in the body is one of the major toxic effects and forms the basis for many treatment recommendations [93]. However, binding to other elements such as K^+ and Na^+ can also occur. Unless surface F^- are neutralized by formation of salts of Ca^{2+} or Mg^{2+}, necrosis is bound to progress. Neutralization can be done topically or intravenously by administering compounds (often propionates) of Ca^{2+} or Mg^{2+}. Hemodialysis treatment is effective for severe systemic fluoride intoxication [100].

Fluoride ion penetration, including its reaction with Ca^{2+} and Mg^{2+}, leads to conditions of hypocalcaemia [101] or hypomagnesaemia. Hypocalcaemia or hypomagnesia if not reversed will eventually lead to nerve failure and cell membrane collapse and eventually to death [102]. Fatal cardiac arrhythmias and severe multiple organ failures have been reported [91].

The concentration of HF dictates the severity of burns [103]. Equally important are the nature of the exposed area and duration of exposure [104]. At concentrations >50%, burns appear immediately accompanied with rapid damage as evidenced by discolouration, usually proceeding to blisters, accompanied by a severe pain [105]. Concentrations of between 20 and 50% can lead to delayed response of up to 8 h, whereas concentrations <20% can lead to effects being felt after about 24 h [106]. Dilute HF solutions (<3%) mostly take longer (>24 h) for the effects to be felt. Dilute HF solutions are normally used in cleaning agents or car wash solutions at professional car wash facilities.

Skin burns with areas >160 cm^2 have the potential to cause serious systemic fluoride toxicity from interference with blood and tissue Ca^{2+} levels [26]. Thus, HF exposure is often treated with calcium gluconate, a source of Ca^{2+} that sequesters the F^-. HF chemical burns can be treated with a water wash and 2.5% calcium gluconate gel or special rinsing formulations [26,107]. In cases of cutaneous exposure, treatment with 10% calcium gluconate and 50% dimethyl sulfoxide for rapid dermal absorption is recommended [108]. Medical treatment may be necessary if these topical treatments are not enough [109].

The Immediately Dangerous to Life and Health HF exposure limit, set by Occupational Safety and Health Administration (OSHA), is <30 mg/L (U.S. Department of Labor (OSHA), 1997). OSHA requires medical surveillance of those working closely with HF. Medical evaluations on skin, eyes, liver, kidneys, and respiratory system are advised before a worker is placed on the job. Health interviews and physical examinations are periodically done during the time of employment. Another medical examination (i.e. urinalysis) follows to determine any effects of the working conditions when the worker is transferred or terminated. The National Institute of Occupational Safety and Health (NIOSH) has also established the level at 30 mg/L that is Immediately Dangerous to Life (IDL) [110]. The American Industrial Hygiene Association has published an *Emergency Response Planning Guideline* setting of 50 mg/L as the maximum HF concentration below which nearly all individuals could be exposed for 1 h without experiencing or developing life-threatening health effects. Recently, 20 mg/L is set as the maximum HF level below which nearly all individuals could be exposed for 1 h without developing irreversible health effects or symptoms that would impair taking protective action [111].

Whereas most of these industries regulate minimal human exposure, some workers in the trucking industry made it a practice to use HF in their cleaning solutions without knowing its hazards or growing regulations. A frequently used mixing method for soap companies in wheel cleaners supplying HF combines it with mineral acid, thus creating a superacid system [112,113]. This can result in acid strengths of up to 12× higher than either acid by itself. There have been reported accidents pertaining to car wash workers afflicted with cleaners containing HF. To mention a few, for example, a certain worker experienced delayed but severe tissue burns after spilling cleaning solution containing 2% HF on his feet [114]. Another car wash worker had her fingers amputated after using gloves contaminated with HF [114].

As the HF-based cleaning solutions are generally cheaper than safer soap alternatives, the cost associated with personal protective equipment appropriate for handling HF outweighs such savings. According to NIOSH and the Centers for Disease Control, permanent blinding can result from exposure to the eyes or eyelids upon contact with HF. OSHA recommends the use of safety goggles with a safety face shield and a respirator when handling HF in any capacity. Chemical cartridge respirators, gas masks, or any equipment supplied such as air respirators with a full mask, helmet, or hood, are approved for handling HF. Spill-proof lab coat, gloves, sleeve covers, and boots should be made of acid resistant neoprene or polyethylene material. In solutions with HF concentration of $\geq$30%, HF has a breakthrough time of 1–4 h for neoprene and polyethylene [115].

In summary, a periodic educational programme and safety training must be instituted so that all workers have the current knowledge of the dangers with regard to handling HF [116]. Although the International Carwash Association is committed to informing the professional car wash community and public about safety concerns related to the use of chemicals in the industry, it does not take a stand to the use of any particular chemical product and is not equipped to monitor the use of any particular chemical.

9. Environmental impact and regulations regarding car wash source and wastewater

The growing public health concern for the water supply derived from streams, rivers, and waterways has led to a number of environmental regulations to protect drinking water and watersheds. Car wash facilities continue to become increasingly regulated in the quest for a clean environment and the demand for a safe workplace. The primary environmental considerations for car washing are the use of water and energy resources [117], and direct or indirect contamination of soil, groundwater, and surface sediments and water [118–120]. A previous study reported that 170 L of fresh water is required for a full-service wash per small car generating wastewater containing high contaminant loads (average concentrations: 1100 mg/L oil and grease, 4500 mg/L chemical oxygen demand, and 3500 mg/L total suspended solids) [121]. Contamination of surface water arises from the rinsate discharges to storm water drains or networks. Water and contaminants that enter storm drains do not undergo treatment and are released into rivers, streams, and lakes [122,123]. Car wastewater can also contaminate soil and groundwater during surface runoff. This is always a concern for driveway washing and moving charity car wash [10].

The sources of pollutants in water from car washing include traffic pollutants, materials from the car itself, and chemicals used for cleaning [124]. Car wash wastewater is therefore complex as it contains many pollutants including HF, ammonium bifluoride (NH_4HF_2), detergents/surfactants, oil and grease, volatile organic and sulfur compounds, polycyclic aromatic hydrocarbons, P and N compounds, chlorinated solvents, paint residues, plasticizers, rubber, rust, phthalates, phosphates, diesel exhaust particles, road grime, and heavy metals from brake pads [125–127]. These pollutants are detrimental to the ecosystem if discharged untreated either into municipal sewage treatment plant [128]. HF, NH_4HF_2, and solvent-based solutions are harmful to humans, plants, and animals. Excess fluoride salts in the environment is also a concern [129]. Professional car washing has the ability to capture these contaminants and have them undergo treatment before being released into sanitary systems. However, pre-treatment processes for car wash stations may not be sufficient to meet water quality standards to discharge wastewater into storm water networks [130].

The use of HF in car wash cleaning solutions is linked to the presence of metal ions found in resulting wastewater. Water quality testing on wastewater samples from self-serve, in-bay, and conveyor car wash operations in Phoenix, Florida, and Boston (U.S.) were conducted [122]. The metals quantified were those commonly found in paints, rubber products, and brake pads of motor vehicles. Sn, As, Cd, Cr, Cu, Pb, Ag, Ni, and Zn were detected in all sites but Be, Hg, Se, and Tl were only detected within the procedural quantitation limit.

A number of European countries have introduced legislations for water use reduction and wastewater recycling associated with car washing. For instance, 60–70 L/car is the maximal fresh water consumption enforced in the Netherlands and the Scandinavian countries, >80% is the wastewater recycling percentage imposed in Germany and Austria, and ~15% of car wash facilities in Belgium reuse 55% of their wastewater nowadays [117].

Companies that operate a fleet of transportation vehicles are always faced with environmental compliance issue on state and federal environmental precautionary regulations. The U.S. EPA established transportation equipment and vehicle cleaning, and developed pre-treatment standards for new and existing sources that discharge Publicly Owned Treatments Works. For example, the Resource Conservation and Recovery Act (RCRA) advises on recycling, treatment, and disposal methods that can minimize HF waste after fleet washing. RCRA recommends installing a closed washing and rinsing system to recycle wastewater while reducing water usage. This system also prevents residue accumulation that creates hazardous wastewater. Reusing the wastewater solutions and applying them as the initial rinse in cleaning another vehicle is suggested. It is also suggested to use waste alkaline solutions to neutralize HF wastes prior to further treatment in units regulated under the Clean Water Act. Moreover, a car wash facility needs authorization through the Clean Water Act before it can discharge wastewater to local sewer or oil-separator systems. The local government pre-treatment standards determine the types and volume of wastes allowed to enter the sewer systems.

10. Recommendations and possible alternatives to hydrofluoric acid

Cleaning an automobile is a laborious and time-consuming task, thus creating a demand for HF, the most effective acid cleaner ingredient that is currently available in the market. Due to hazards associated with storage, use, and exposures of HF, efforts are being directed to develop new alternatives. An ideal chemical to replace HF should have the following characteristics: effective without the need for further scrubbing, reacts rapidly with dirt but does not necessarily require elevated temperatures to work, cleans the surface without pitting, etching, or hazing, and does not strip paint or leave an insoluble residue.

Many soap companies have recommendations on how to use their products containing HF when cleaning automobiles. A two-step automatic drive through process can be adopted. This process involves the application of an HF-based cleaning solution to first to "shock" the surface and loosen up soil, grease, and oils, and then adding an alkaline solution to balance the acidity before it starts to corrode the surface. Other soap companies recommend using old-fashioned elbow grease with a scrub brush. One soap company specifies using an alkaline soap with HF when manually applying the acid. Another alternative cleaning method suggested is to clean from the bottom surface up while rinsing in order to prevent corrosive streaks.

Below are the specific methods and chemicals as 'alternatives' for HF in car wash cleaning solution:

- Improved washing method: The use of more traditional detergents in addition to mechanical methods, either water jetting or physical brushing of wheels to remove brake dust, is common in Europe. One such example was having a mild pre-wash solution sprayed onto the wheels, which are then sprayed with high-pressure water jets and further cleaned with revolving brushes. While the mechanical design of car washing systems may improve the effectiveness of the less aggressive cleaning products, this is not viewed as a viable option to replacing HF as an ingredient in a brushless car wash application.
- Water pre-treatment: Another possible alternative to HF is the development of an improved process of car washing by pre-treating the wash water prior to application to the automobile. Pre-treatment includes increasing the temperature of water or cleaning solution used for the initial rinsing, or modifying its properties to improve washing efficiency and chemical reactivity.
- Polymer lifting: S & S Car Care, Inc. introduced cleaning products which lift dirt from car wheels rather than dissolving it off [131]. The thought of a spray-on polymer solution, which would bind with the brake dust on the wheel and then be peeled off, is a potentially novel solution to the cleaning and water usage problems. Similarly, the car washing business Keenwash, recently introduced a non-toxic, almost biodegradable, and cheap spray-on carwash fluid in water-scarce countries in the Middle East [4]. Both of these products would work well in the Do-It-Yourself market, but may not be practical for automated car wash operations.
- Ammonium bifluoride: Instead of HF, NH_4HF_2 and H_2SO_4 can be added to acid Al surface cleaner/surfactant and water [132]. NH_4HF_2 has been touted as a safer alternative for HF than additives or chemicals in some car wash cleaning applications. This is a dangerous misconception since NH_4HF_2 essentially dissociates into HF when dissolved in water. NH_4HF_2 is therefore not recommended to be considered as an alternative for HF.
- Cleaning solutions in various recent patents: The latest advances in HF replacements for car wash applications were mostly found in the patent literature. Ecolab, Inc. in St. Paul, Minnesota has a recent U.S. patent for a car wash cleaning solution which specifically states that it uses less aggressive materials than HF [133]. The car wash cleaning solution is composed of an anionic surfactant, poly(oxyalkylene) ammonium surfactant, and an alkaline agent. Cleaning Systems Inc. in De Pere, Wisconsin produces the Lustra® line of car wash cleaning products. This company was granted a U.S. patent in 2009 for a metal brightener and surface cleaner which is safe for other surfaces such as painted surfaces, glass, rubber and plastic [134]. The cleaning product is composed of an alkali metal hydroxide, a polycarboxylic acid, an alkali metal salt of an organic acid, and various surfactants. The company describes the alkali metal hydroxide as being sodium or potassium hydroxide, the alkali metal salt as being sodium glucoheptonate, and the polycarboxylic acid as ethylenediamine tetraacetic acid or propylenediamine tetraacetic acid. Shell Oil Company in Houston, Texas holds a patent for an aqueous wheel cleaner for automobile tires. The cleaning solution is composed of an alkylene glycol, a salt of dialkyl sulfosuccinate, and ethanolamine and an ethyloxylate phosphate ester surfactants [135]. Ashland, Inc. in Covington, Kentucky has a number of patents on a touchless wheel and tire cleaner composition which makes use of vinylpyrrolidone, vinyimidazole, and vinylpyridine polymers as chelating agents to bind on dirt particles [136]. The product makes use of a combination of acids such as HF, HCl, H_2SO_4, HNO_3, oxalic, acetic, nitric hydroxyacetic, and citric acid. Henkel Corporation in Plymouth, Pennsylvania has a U.S. patent for a cleaning solution to be used on soiled railway cars which contains acid fluoride ions (HF_2^-) not derived from hydrogen fluoride [137]. The patent claims that the solution will not etch glass but can be applied on unpainted metal surfaces such as those of stainless steel and Al.

Other types of cleaning formulations have been devised and patented for use on metal surfaces and industrial machinery. However, such compositions generally have to be used at elevated temperatures and typically work by etching the surface to be cleaned. For example, in U.S. Patent No. 3,969,135, NH_4F was used in cleaning formulations for the removal of residues on Al surfaces that remain after the production of the metal [138]. To be effective, the cleaning composition was used at elevated temperatures (322 K). In U.S. Patent No. 4,346,128, a tank process for plating aluminium Al substrates is described [139]. The process involved a cleaning step of immersing the substrate in a low pH dilute acid bath containing an acidic fluoride-containing salt so as to remove surface contaminants such as heavy oxides and silicon from the substrate. However, this cleaning process resulted in some etching of the Al substrate. The U.S. Patent No. 4,614,607 describes a deoxidizer gel comprising an aqueous solution of HNO_3, H_2SO_4, NH_4HF_2, and fumed silica which cleans Al by way of a constant etching rate [140]. The composition effectively removes oxides, scale, corrosion, and residual matter before anodizing the Al alloy surface. The U.S. Patent No. 5,733,377 details a dual approach of the organic compound cleaning product (detergent/organic solvent) that can emulsify soil and grease and replace HF with a material that can rapidly mineralize metals or metal oxides including calcium fluorophosphates and sodium fluorosilicates [141]. Meanwhile, the U.S. Patent No. 5,932,023 describes an effective formulation of a cleaning product having an acid solution and a fluorine solution [142]. Lastly, the U.S. Patent No. 6,982,241 describes a formulation containing an acid with a $pK_a \leq 2.5$, a H_3PO_4 solution, and an oxidant [143].

11. Conclusions

Wear of brake pads and discs, tire wear, abrasion of road surfaces, soil, and urban pollution are the major sources of particulate matter and their accumulation on automobiles is unpreventable. In this contribution, the basic idea on the use of HF in the car wash industry has been highlighted. The physico-chemical properties and etching chemistry of HF have been discussed. The ability of HF to aggressively clean brake dust and road grime on automotive surfaces is directly linked to this unique chemistry where the components of these particulate matter are readily broken down. The information presented in this literature review suggests that the use of HF as a cleaning agent has indeed a huge impact in the car wash industry.

It is apparent from the literature that HF-containing cleaning solutions, together with the waste reaction products, are considered hazardous. The increased awareness of the public on the effects of HF in environmental health will not necessarily result to a decrease in the use of this chemical. The disposal of car wash wastewater can be difficult; therefore, it is necessary to eliminate the use of HF in car wash applications and to develop effective methods to regenerate car wash cleaning solutions and pre-treat resulting wastewater.

While there are alternative cleaning products available in the market, we have found no published scientific articles in the current and reasonably accessible literature on their effectiveness compared to HF. It is therefore difficult to assess at this time whether any of the possible alternative methods and products could be an effective HF replacement. However, an environmentally safe and non-toxic cleaning agent, combined with high-pressure water cleansing, might be the best alternative for HF use on transportation vehicles. Yet, the expenditure, ingredient sustainability, and water conservation issues need to be addressed. More efficient water reclamation and recycling systems are necessary to significantly reduce water usage. It is also of public interest to see how this conflict between the negative health and environmental aspects, and the relative simplicity of the application of HF-containing car wash cleaning solutions will be resolved.

There may still be no existing chemical compound that can directly replace HF in its ability to remove brake dust and road grime on automobile yet. Due to inherent dangers of using HF, only people who are specifically and thoroughly trained in its proper use and handling, and have the necessary protective equipment to handle the chemical safely should use it. As a matter of policy, car wash cleaning companies should not sell to customers who do not have the specific training on safe handling of HF even at prescribed concentrations. That being said, given the highly toxic nature of HF, the development of safer yet less effective alternatives would be the socially responsible proper choice.

It is our recommendation that companies directly or indirectly involved in car wash industry should strictly implement changes to the car washing process that would eliminate the need to use HF. These companies may start collaborating with local institutions and universities to develop alternative processes and various methods to improve car washing processes, and chemical formulations using the information provided in this review.

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