

Aerosol Forming Compositions for Fire Fighting Applications: A Review

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Abstract. Aerosol forming compositions (AFCs) have come up as one of the most efficient fire extinguishing Halon alternative since the implementation of Montreal protocol-1987 on ozone layer depleting substances. These aerosol based systems have gained much attention in recent years because of higher fire extinguishing efficiencies, modular nature, non pressurized container, less maintenance requirement, extended shelf-life and negligible ODP, GWP and ALT values. Aerosols are traditionally produced using pyrotechnique compositions having mostly metal salts of group IA or IIA. Potassium nitrate has been used predominantly as oxidizing agent $(40-75\%, w)$ w), whereas for electric and electronics systems, strontium nitrate $(15-70\%, w/w)$ has been recommended. Versatile reducing agent, binders, gas forming agents, burn rate modifiers and many such functional additives have been used recently for preparations of AFCs. AFCs indicated variable burn rate values, 2–7 mm/s. AFCs were found highly efficient with minimum fire extinguishing concentrations mostly ranging between 30 $g/m³$ and 200 $g/m³$. Moreover, the development of highly efficient, noncorrosive, non-toxic and environmentally benign AFC is still an elusive goal. This review mainly focuses on advances of aerosol forming chemical compositions, its future prospects and potential research areas.

Keywords: Aerosols, Fire extinguishing, Redox reaction, Pyrotechniques, Burn rate

Abbreviations

AFC_S	Aerosol forming compositions		
CAFES	Condensed aerosol based fire extinguishing system		
ALT	Atmospheric life time		
DCDA	Dicyandiamide		
GWP	Global warming potential		
HMTA	Hexamethylenetetramine		
ISO	International Organization for Standardization		
MMAD	Mass median aerodynamic diameter		
ODP	Ozone depletion potential		
PFR	Phenolformaldehyde resin		

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PTFE Polytetrafluoroethylene US EPA Unites States Environmental Protection Agency

1. Introduction

Montreal Protocol-1987 brought out the protective actions for ozone layer and promoted the phase out of Halon (1301-CF₃Br,1211-CF₂ClBr, etc) fire extinguishants due to their high ozone depletion potential (ODP). Fluorinated chemicals $[FM200-CF_3CFHCF_3, Novec-(CF_3)-CFCOC_2F_5, etc]$, dry chemicals, carbon dioxide, water mist, inert gases (N_2, Ar, etc) (Fig. [1\)](#page-2-0) have gained much attention in recent years as Halon alternatives for fire fighting applications [\[1–4](#page-27-0)]. These agents involve the phenomenon of heat removal (cooling/decomposition), oxygen depletion (dilution/suffocation) and chemical reaction inhibition for fire extinguishment. Fire extinguishing properties of various agents along with their environmental parameters is provided in Table [1](#page-3-0) [\[5](#page-27-0), [6](#page-27-0)]. Fluorinated fire extinguishants are lesser efficient than Halon, has high global warming potential (GWP) and also produces hydrogen fluoride, which is highly corrosive through both respiratory tract as well as through skin penetration. Inert gases, carbon dioxide and water mist are promising, but required in large quantities with hefty storage systems. Dry chemicals $(25-150 \mu)$ and wet chemical foam extinguishers sprayed directionally onto the fire, left more residue post fire extinguishing, and attract complicated cleanup procedures. Therefore, the search on an efficient, simple and environmentally benign fire extinguishing technology is under way since the agreement of Montreal protocol.

Condensed aerosol based fire suppressing technology has emerged as one of the most suitable Halon alternative due to its superior fire extinguishing efficiency, minimum environmental impact, nil toxicity and low residue. This technology evolved during the Soyuz rocket programme in Soviet Union [\[7](#page-27-0)]. Condensed aerosol based fire extinguishing technology has progressed from potassium nitrate based K-type [generation-I (oil tank fire suppression for class B only) and generation-II (for class A , B , C , E and K)] systems to strontium salt based S-type generation-III (for class A, B, C, E and K) systems, Table [2](#page-4-0). Compared to potassium based K-type generation I and II systems; S-type condensed aerosol fire extinguishing technology greatly solves the problem of corrosion for electronic and electrical devices.

Basically, condensed aerosol based fire extinguishing system (CAFES) contains the solid aerosol forming composite (AFC) comprising of oxidiser, reducer, binder and technological additives. Apart from the required function characteristics, these chemicals need to be non toxic for the overall safety of the AFC. Table [3](#page-5-0) provides the physico-chemical properties and GHS classification of various ingredients of AFCs. Zhang et al [\[8](#page-27-0)] has given the details on variety of ingredients of AFCs. Anhydrous and non-deliquescent chemicals are the choice as AFC ingredients. Tables [4,](#page-7-0) [5](#page-8-0), and [6](#page-9-0) represent the classification of AFCs based on various oxidizing agents. The oxidiser may involve the nitrates, halogenic acid salts, perchlorates, perbromates, periodates or chlorates, bromates and iodates of alkaline metals, alkaline earth metals and transition metals. Potassium nitrate and Strontium

Figure 1. Categories of fire extinguishing agents.

nitrate have been largely used as promising oxidiser. AFCs contain potassium nitrate either as single oxidiser or in conjugation with other oxidizers. Chemicals which produce large amount of incombustible gases are preferred as reducing agents. It mainly involves carbohydrates, metals, carbons and guanidine derivatives. Epoxy and phenol formaldehyde have been used as the most common binder. Binders can also act as reducing agents. Technological additives are also added in AFC to impart the features, viz., smoothening, stabilization, moisture protection, long storage life and low toxic by-products. AFC on combustion may produce particulate matters (K₂CO₃ and KOH) of size < 10 μ m, inert gases/vapours $(CO_2, H_2O$ and N_2) and sometimes small amount of toxic gases (HCN, $NH₃$, CO, NO_x, etc) under specific fire conditions. The generalized chemical reaction of AFC is:

$$
MNO_{3(s)} + C_nH_mN_pO_{q(s)} + C_{(s)} = MHCO_{3(s)} + M_2CO_{3(s)} + CO_{2(g)} + N_{2(g)} + H_2O_{(g)}
$$

(where $M = Na$, K, Mg, Ca, Sr or Al).

The combustion of AFC can be initiated manually or automatically using internal thermal or electrical ignition mechanisms. At the fire zone, the particulate matter, mainly composed of potassium carbonate decomposes to produce potassium radicals, which in turn react with fire sustaining radicals. These interactions break the chain reaction of fire and extinguish it.

Fire Extinguishing Characteristics and Environmental Impact of Different Fire Fighting Agents (Solid, Liquid and Gases)

Micron size aerosol particles can cause adverse health effects once inhaled. Because of the toxicity issues, US EPA has approved CAFES for non-occupied or not normally occupied areas [\[9](#page-27-0)]. Some of the countries like Russia, United States of America (USA), Australia and China have already developed standards and norms for manufacturing and quality control of AFC and CAFES for different fire protection scenarios, Table [7](#page-11-0).

Overall, the aerosol based fire fighting technology is a fast, reliable and leading technology, which is four times more effective than Halon per unit mass and can extinguish A, B, C, D and K classes of fires. Aerosol based composites are non toxic, cost effective and environmentally safe with (negligible GWP, ODP and ALT-atmospheric life time) [\[10](#page-27-0)]. CAFES can extinguish fire at 30 to 200 g/m³ design concentrations of AFC [[8\]](#page-27-0). The technology has not been widely utilized but its simplicity and effectiveness attracts widespread applications. Moreover, the development of highly efficient, non-corrosive, non-toxic and environmentally benign AFC is still required. The current review chiefly focus on the critical evaluations of AFC composition developed worldwide for fire extinguishing applications.

Table 1

S. no.	Type of system	Ingredients	Type of agent/generation	Application
1	G1	Potassium nitrate	K-type (partially generated) in generator)	(Class B fire only) Tank liquid fires such as oil, alcohol and ketone flames
	G ₂	Potassium nitrate	K-type (fully generated in generator)	(Class A, B, C E and K) Engine compartment, warehouse, Machinery space
	G ₃	Strontium nitrate or Magne- sium nitrate	S-type (fully generated in generator)	(Class A, B, C E and K) Electronics and electrical appliances

Table 2 Different Generations of Aerosol Based Fire Extinguishing Technology

2. Ingredients of Aerosol Forming Composition

Aerosol forming compositions are the mixture of oxidants, reductants, binders and technological additives. The basic requirement for AFC ingredients is to be non-hygroscopic, non-deliquescence, least degree of hydration, gas forming, minimum residue and non toxic. Table [3](#page-5-0) represents the physico-chemical properties and GHS classification of ingredients of aerosol forming compositions. The most important ingredient of AFC is oxidizing agent.

2.1. Oxidizing Agents

Oxidizing agents are generally oxygen-rich ionic solids, which readily decompose to release oxygen at high temperatures. An oxidizer must possess high oxygen content, low heat of formation, high density, good operational thermal stability and low hygroscopicity. Suitable oxidants have negative ions possessing high-energy Cl–O or N–O bonds, e.g., nitrates, chlorates, perchlorates, etc. Halogen containing salts (halogenic acid, chlorates, perchlorates, etc) of group IA elements are all anhydrous but deliquescent and highly reactive. These can be used as secondary or minor oxidants. Halogen containing salts of group IIA, IIIA or transition metals are either highly hydrated or hygroscopic, and they are relatively expensive, hence not considered. Nitrates have been considered as the most effective anions for oxidant. During combustion metal nitrates are converted to oxides, carbonates and hydroxides. These, when come in contact of fire, produce metal radicals, which recombine with H and OH fire propagating radicals and subsequently extinguish the fire. Chlorides were more active for recombination of O radicals [\[11](#page-27-0)]. Effectiveness of hydroxides was higher than for carbonates.

The alkali metals and alkaline earth metals have been considered because of their poor electron acceptors characteristics, non reactivity towards active fuel metals (Al, Mg, B, etc) and anhydrous nature. The order of fire extinguishing efficiency for alkali metals was $Cs > Rb > K > Na > Li$ [\[11](#page-27-0), [12](#page-27-0)]. Since cesium and rubidium salts are costly, sodium and lithium salts are hygroscopic, hence,

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×

Causes severe skin burns and eye damage Causes severe skin burns and eye damage 13 Potassium oxide 740 350 GHS05—Corrosive H314—Causes severe skin burns and eye damage H314—Causes severe skin burns and eye damage May cause respiratory irritation May cause respiratory irritation H335—May cause respiratory irritation H335—May cause respiratory irritation Flammable liquid and vapour 11 Nitrocellulose 160–170 – GHz and vapour Hammable H226—Flammable H226—Flammable liquid and vapour liquid and vapour -Harmful in contact with skin H312—Harmful in contact with skin GHS hazard statement Causes serious eye irritation Causes serious eye irritation temperature (C) GHS classification GHS hazard statement H319—Causes serious eye irritation H319—Causes serious eye irritation Causes serious eye damage H316–Causes mild skin irritation H318—Causes serious eye damage H316—Causes mild skin irritation Harmful if swallowed Causes skin irritation Harmful if swallowed Causes skin irritation H302-Harmful if swallowed 204 GHS07—Harmful H302—Harmful if swallowed 12 Potassium carbonate 891 891 GHS07—Harmful H302—Harmful if swallowed H320–Causes eye irritation H302—Harmful if swallowed Causes eye irritation H315—Causes skin irritation H315—Causes skin irritation H320—Causes eye irritation 14 Potassium bicarbonate 292 292 GHS07—Harmful H320—Causes eye irritation Toxic if inhaled H331—Toxic if inhaled $H314 \frac{1}{2}$ GHS05-Corrosive 15 Potassium hydroxide 360 – GHS05—Corrosive GHS07-Harmful GHS07-Harmful GHS07—Harmful 292 Ï 292 360 Potassium bicarbonate Potassium hydroxide

 $15 \,$

 $\overline{1}$

Table 4 AFCs having Potassium Nitrate as the Single Oxidising Agent Along with Reducing Agents, Binders and Technological Additives, and Their Characterizations

Table 6
AFCs having Strontium Salts, Reducing Agents, Binders and Technological Additives, and Their AFCs having Strontium Salts, Reducing Agents, Binders and Technological Additives, and Their

scopicity, ease of ignition of mixtures containing it [[15\]](#page-27-0).

potassium salts could be the most suitable candidate. Among alkaline earth metals, nitrates of barium and beryllium are toxic. $Sr(NO₃)₂$ is the most suitable due to its higher stability and least deliquescence tendency. Nitrates of group IIIA, IVA, VA and transition metals were mostly unstable/deliquescent/hydrated/toxic. Zinc and copper nitrate can be used to enhance the fire extinguishing efficiency of AFC [\[13](#page-27-0), [14](#page-27-0)]. The amount of oxidizing agents is to be optimum as the AFCs with coefficient of oxygen balance less than one may possibly increase carbon monoxide concentrations in protected enclosure [\[12](#page-27-0)]. Overall, potassium nitrate has been widely considered because of its readily availability, reasonable cost, low hygro-

2.2. Reducing Agents

Reducing agents are also known as fuels in the field of pyrotechnics/propellants. Reducing agents in AFC are the electron donor species, which react with the liberated oxygen in the form of combustion and release heat. This heat is further utilized in commencement of the redox process. The combustion mainly produces solid particulates (aerosols) and incombustible gases. Chemicals, which can produce incombustible gases in huge quantity during combustion, are considered as the most suitable reducing agents in AFC. A variety of chemicals can be selected as reducing agents considering the factors, viz., stability, reactivity, amount of heat released, toxicity, cost and amount of gaseous products. Reducing agents can be divided into three broad categories, viz., organics, metals and non metals. Organic reducing agents include polymers, carbohydrates and nitrogen containing compounds (e.g., derivative of guanidines and tetrazoles).

Derivatives of guanidines such as nitro guanidine and dicyandiamide have been considered the most because of production of large quantities of nitrogen during combustion. The only limitation of use of guanidines is the risk of generation of hydrogen cyanide because of incomplete combustion. This can be controlled using technological additives supporting the complete combustion or performing chemical neutralization. Derivatives of tetrazoles have also been considered to produce large quantities of nitrogen gas, but the limitation is lower stability and safety issues. Polymers like phenolic resins, acrylic resins, epoxy resins, polyvinyl alcohol and unsaturated polyester resins have been used as reductants [\[16,](#page-27-0) [17](#page-27-0)]. These polymers on combustion produce carbon dioxide and water vapour. Denisyuk et al [[17\]](#page-27-0) has also discussed the use of cyanuric acid, barbituric acid or hydroxyacetic acid salts of alkaline metals and alkaline earth metals as low heat reductants. Carbohydrates (lactose, sucrose, cellulose and its derivatives), charcoal, carbon black, stearic acid, hexamethylenetetramine (HMTA), kerosene, aluminum, magnesium, sulphur, etc. have also been utilized as reducing agents.

2.3. Binders

Binder is a substance used for adhesion of particles and uniform solidification of the ingredients. The role of a binder is to hold all the components together in a homogeneous blend and provide good mechanical strength and structural integrity to the composite. Without the use of a proper binder, ingredients might well segregate during preparation and storage due to variations in density and particle size. Basically, the binders are organic compounds, which also serve as fuel in the mixture. Epoxy and phenolic resins are the two most common binders used in AFC; others can be hydroxyl terminated polybutadiene (HTPB), nitrocellulose, polyethylene, fluoroplastics, iditol and melamine [\[18](#page-27-0)]. Organic binders, when used alter the combustion process and induce new exotherms, leading to significant reduction in the ignition temperatures of the AFC [\[19](#page-27-0)[–22](#page-28-0)]. Moreover, for the preparation of AFC, binders are usually solubilized in appropriate solvents and thereafter oxidizer, fuel and other components are blended to it to produce homogeneous composition.

2.4. Functional Additives

Additives are the auxiliary compounds that are added in AFC to tune its properties and produce the required effect. Additives can function as processing aids, fluxing agents, thermal insulators, sensitizers, catalysts and heat sinks [\[23](#page-28-0)]. The role of additives include the stabilization of redox process, enhancement of the storage life, control of burn rate, reduction in friction, decrease in ignition temperature, reduction in concentration of toxic gases, keeping the AFC block dry and prevent it from moulding. Zhang et al [[24](#page-28-0)] has discussed the role of oxides/carbonates of group IA/IIA elements to slow down and smoothen the redox rate, and oxides of transition metals (Cu, Ni, Mn, Fe and Cr) to catalyze the reduction of carbon and nitrogen mono oxides in the aerosol gas phase. Sodium azide has the potential to be used as burn rate modifier in AFCs because of high density, high burning rate, short induction period on ignition and non-toxic gas formation properties [[25\]](#page-28-0). Stearates are used to keep the AFC dry, prevent it from growing deformation and enhance the storage life. Beck et al [\[26](#page-28-0), [27\]](#page-28-0) suggested to modify the burn rate of a binary system by conversion to a ternary system through incorporation of additives.

3. Preparation of Aerosol Forming Compositions

AFC preparation process involves the grinding of ingredients, homogenous mixing, coating, drying and moulding (Fig. [2](#page-14-0)). In one of the process, oxidiser (potassium nitrate, $67-72\%$ w/w) and reducer (melamine, $9-30\%$, w/w) were pulverized to 80–200 standard sieve mesh and mixed homogenously in specified proportions [\[28](#page-28-0)]. To this, the solution of binder (phenolic resin, $8-11\%$, w/w) in ethanol was added and the mixture was agitated for a specified time. Thereafter, the composite was sieved (40 mesh sieve), dried (40 $^{\circ}$ C and 20% relative humidity) till the volatile constituents reached below 1.0%, and finally, shaped by pressure moulding at 10 MPa. Valeriy et al [[29,](#page-28-0) [30](#page-28-0)] prepared AFC by through mixing of all ingredients $(15-100 \mu m)$ in the solution of phenolformaldehyde resin (PFR, dissolved in ethanol and acetone in a ratio of 50:50). Water based compositions have also been prepared by mixing all ingredients in water to form homogenous composite [[31\]](#page-28-0).

A complete preparation of AFC and the importance of particle size of ingredients have been discussed by Drakin et al [[32\]](#page-28-0). Here, all ingredients were taken in

Figure 2. General process of preparation of aerosol forming composition.

two size fractions, viz., gas forming agent $(40-80$ and $7-15$ µm particles in a ratio of 80:20); binder (70–120 and 10–25 μ m particles in a ratio of 70:30) and oxidiser (15–25 and 1–7 μ m particles in a ratio of 25:75). Large and small particles combination was found helpful in close packing of the components, wherein the large particles form the framework and the smaller particles fill into the intermediate spaces between them. Close packing of the particles helped in getting stress less composite with total linear combustion performance. Combustible binder can also be added as solution phase in appropriate solvent. Coating of combustible binder resins on ingredient particulates help in reducing the required moulding pressure due to easy moment of particles in the flow at the application of stress. Efficient packing of the ingredients makes it possible to use more Oxidizing agent, which in turn produce more aerosols. To increase the burn rate of AFC, ammonium dichromate or potassium chromate or potassium dichromate (1.0–3.5%, w/w) can be coated over Oxidizing agent particles prior to mixing. Due to this coating, at the ignition of the composition, the heat front propagates within its volume and facilitates the thermal decomposition of oxidiser.

Graphite powder $(0.2-0.5\%, w/w)$ has been added at the time of grinding with some portion of Oxidizing agent. While grinding, under shearing forces, graphite disintegrates and easily applied over the surface of Oxidizing agent particles. It imparts the hydrophobic properties to the AFC and also functions as lubricant, which reduces the surface friction and in turn reduces the moulding pressure.

Most importantly, graphite is located directly on the heated layer of the decomposed potassium nitrate and diffuses into the gas zone of the flame, where it interacts with the decomposition products, performs endothermic reactions and reduces the combustion temperature of AFC.

Aerosol forming compositions are basically pyrotechnique mixtures, which require special care during handling. As a caution, major factors namely pressure, temperature, static charge and friction need to be considered while preparing AFCs. The work should be performed at low temperature and pressure. Proper static charge neutralizing devices and friction less processing aids should be used.

4. Categorization of Aerosol Forming Compositions

Variety of AFCs has been prepared worldwide. The most important ingredient of AFC is the oxidizing agent, which is taken in highest amount. Therefore, in this review AFCs have been categorized into four categories on the basis of oxidizing agents alone.

4.1. Potassium Nitrate as Oxidizing Agent

Potassium nitrate has been considered as the most promising oxidizing agent worldwide due to its readily availability, reasonable cost and low hygroscopicity. 40–72% of potassium nitrate has been used in AFCs [\[28–40](#page-28-0)], Table [3.](#page-5-0) Melamine, dicyandiamide (DCDA), dicyanamide, guanidine nitrate, sucrose and carbon black have been used as reducing agent within 9–60% in aerosol producing formulations. The burn rate of AFCs has been regulated using various catalysts.

AFCs have been prepared using melamine $(20-30\%, w/w)$ as reducing agent [\[28](#page-28-0)]. Much emphasis is being given on not to use highly active ingredients, e.g., chlorates, perchlorates, dicyandiamide, etc. Highly active ingredients degrade the aging resistant performance of AFC and dicyandiamide lowers the gas yield rate of AFC. Higher suppression efficacy $(20-25 \text{ g/m}^3)$ and higher aging resistant performance (10 years) has been claimed. Dicyandiamide $(9-16\% \,$, w/w) has been used as dry propellant, which functions as reducing and gas forming agent to pro-duce nitrogen gas on expansion [\[29](#page-28-0)]. Phenol formaldehyde resin $(8-12\% , w/w)$ was used as binder cum reducing agent. AFC composition also contained minerals/vitreous granulates of size 0.2 mm, benzoate, bicarbonate and hexacyanoferrate as additives. Composition having potassium nitrate $(70\%, w/w)$, phenolformaldehyde resin (10%, w/w), dicyandiamide (10%, w/w) and potassium bicarbonate (10%, w/w) showed highest discharge (99%) and required lowest fire extinguishing concentrations (22 $g/m³$) [\[30](#page-28-0)]. The compositions also indicated 1.8– 2.5 mm/s as speed of fire, 53–64 mol% as yield of dispersed phase with traces of ammonia and nil carbon dioxide. Applications in aero plane engines, ships and plants endangered by fire and explosion have been suggested. Toxic gases produced during combustion of the AFC have been identified using gas chromatograph-thermal conductivity detector (CO and CH4) and colorimetric technique (NH₃, NO_x and HCN) [[32\]](#page-28-0).

Apart from phenolformaldehyde resin (10–15%, w/w), epoxy resin (10–40%, w/ w) or ballistic powder (55–60%, w/w) has also been used as binder/fuel [\[33](#page-28-0)]. The compositions could produce $64-75%$ mass fraction of $1-2 \mu m$ particles with fire extinguishing concentrations of $40-76$ g/m³.

To ensure close packing, ingredients (potassium nitrate, phenol formaldehyde and dicyandiamide) in various particle sizes have been considered for the preparation of AFC [[34\]](#page-28-0). Melamine formaldehyde resin or carbamide formaldehyde resin $(11\%, w/w)$ has also been used as binder [\[34](#page-28-0)]. The compositions also had potassium dichromate and graphite in the range of 1.0–3.5 and 0.3–0.5% as burn rate modifier and lubricant respectively. The best composition showed 4.0 mm/s as linear combustion velocity, 650°C as combustion temperature, 32 $g/m³$ as fire extinguishing concentrations and 70% of 1–2 μ m particles in dispersed phase. Higher amount of guanidine nitrate $(42-60\%, w/w)$ with polyvinyl alcohol (PVA) $(1-3\%,$ w/w) has been considered to get compositions with low flame temperature, low pressure and high burning rate [[35\]](#page-28-0). Iron oxide nanoparticles (surface area, 250 m²/g and density, 0.5 g/mL, amount, 0.5%, w/w) singly or in combination with copper phthalocyanine $(2.0\%$, w/w) have been considered as burn rate modifier. The compositions exhibited increased burning rate (2.0 to 20.0 mm/s) with an increase in pressure.

Mikhailov et al [[37\]](#page-28-0) used cyanuric acid (15–26%, w/w) and urea (1–12%, w/w) to reduce the combustion temperature of AFC. Cellulose paper (30–70%, w/w) or cloth (40–50%, w/w) can also be considered as fuel for low temperature AFCs [\[38](#page-28-0)]. Basically, cellulose consumes relatively large amount of heat during thermal decomposition than the heat produced during combustion (low heat of combustion), all that makes cellulose based AFCs as low temperature flameless compositions. Here, thermal decomposition of cellulose forms a soot skeleton, which activates the decomposition of potassium nitrate. High oxygen content (50%, $w/$) w) of cellulose facilitates in complete oxidation of AFC resulting lesser toxic products. Cellulose can also be coated with nitrocellulose or epoxy lacquers to impart hydrophobic characteristics. Use of nitrates of iron or copper $(5\%, w/w)$ increased the burn rate by 25%. Carbon black (10–12%, w/w) or aluminium (2–8%, w/w) with magnesium carbonate can be used as reducing agent and burn speed regulator respectively [[31,](#page-28-0) [40\]](#page-28-0).

4.2. Potassium Nitrate with Other oxidizing Agents

Various chlorates, perchlorates and carbonates have been used along with potassium nitrate as co-oxidants $[16, 17, 36, 41–45, 49]$ $[16, 17, 36, 41–45, 49]$ $[16, 17, 36, 41–45, 49]$ $[16, 17, 36, 41–45, 49]$ $[16, 17, 36, 41–45, 49]$ $[16, 17, 36, 41–45, 49]$ $[16, 17, 36, 41–45, 49]$ $[16, 17, 36, 41–45, 49]$ $[16, 17, 36, 41–45, 49]$ $[16, 17, 36, 41–45, 49]$, Table [4.](#page-7-0) One of the AFC contained a mixture of sodium nitrate, potassium perchlorate and sodium perchlorate as oxidiser [[36\]](#page-28-0). The AFCs also contained low temperature supplementary fuel selected from carbon free polynitrogen compounds or organic/inorganic azides. This includes melamine, urea, urotropin, dicyandiamide, tetrazole, ditetrazole, semicarbazide, etc. Dicyandiamide concurrently promoted a reduction in the equilibrium temperature of the full oxidation reaction. 4-oxybenzoic acid $(9-17\%, w)$ w), during combustion, supported the formation of carbonic core, which also accelerated the oxidation of under oxidized toxic gases. Oxides of transition metals $(< 5.0\%$, w/w) were used as additives for the reduction of toxic gases, increasing flow property and increasing the burn rate. The fire extinguishing performance of the AFCs has been proven on articles up to 100 kg and more in mass.

Phenolformaldehyde resin has been used in most of the compositions as combustible binder. It has been plasticized by dicarboxylic ester, e.g., dibutylpthalate $(0-4.8\%)$ or dioctylsebacate $(0-6.2\%)$ or mixture thereof and reinforced by polytetrafluoroethylene (PTFE) $(0-5\%)$ [[16,](#page-27-0) [17\]](#page-27-0). A little of stearates (St.) of zinc or sodium or calcium, due to their surface active properties, have been used singly or in combinations to reduce external friction between particulate matters. Potassium perchlorate (20%, w/w) with potassium nitrate (64%, w/w) and additives resulted in AFC with higher value of burn rate (7.0 mm/s) and lowest fire extinguishing concentrations (10 $g/m³$). Moisture content of ingredients has been suggested to keep at minimum, as higher moisture content leads to unsteady inflammation due to impaired adhesion of oxidiser to the polymeric binder surface [\[17](#page-27-0)]. All that also lead to drastic decrease in the strength characteristics of the finished product.

Potassium ferricyanide (5–9%, w/w) has also been used as combustion modifier to attain extinguishing efficiency of $30-40 \frac{\text{g}}{\text{m}^3}$ [\[41](#page-28-0)]. The ratio of binder to oxidizing agent is important; as the insufficient quantity of oxidizer may lead to incomplete oxidation of binder resulting in toxic and explosion hazard by-products. When potassium nitrate is used as an oxidiser, it produces basic potassium hydroxide, which is highly hygroscopic, and can corrode the metals and sensitive electrical/electronic systems. But when magnesium nitrate is used, magnesium oxide is generated, which is water insoluble, hence, causes no secondary damage [\[42](#page-28-0)]. Additional benefit of using magnesium than potassium is its lower atomic weight. The same mass fraction of lower atomic weight element can produce more aerosol particles with quick release. Aluminum, magnesium or their alloys, charcoal, magnesium carbonate, etc have been recommended as performance modifier.

To enable block characteristics and practical utilization purposes AFC are pres-sed at 1500 kg/cm² [\[43](#page-29-0)]. The stickiness of ingredients of AFC can be increased using a mixture of technological additives including lubricant oil, diethylene glycol and a salt of a fatty acid [\[44](#page-29-0)]. Centralite has also been used as a stabilizer for chemical stability and modifier of burn rate. Glycols, used as lubricants cause the lowering in external friction. The best fire extinguishing concentrations achieved was as low as 8 g/m^3 . Gypsum and cement have been used for complete curing of astringent solutions of AFCs [\[45](#page-29-0)].

4.3. Strontium Salts with Other Oxidizing Agents

Aerosol forming compositions composed of potassium nitrate have demonstrated high fire extinguishing efficiencies. During fire extinguishing these AFCs can produce strongly alkaline K_2O , which easily melt in water and generate a strong alkaline and conductive aqueous solution of potassium hydroxide that can cause secondary damage to the spaces to be protected. Therefore, potassium nitrate based AFCs are not recommended for electronic/electrical fire. Strontium nitrate has been suggested as the alternate of potassium based oxidizing agents because the solid particulates produced in the aerosol consist of strontium oxide and strontium carbonate, which are quite stable and insoluble in water and does not lead to corrosion [\[46](#page-29-0), [47](#page-29-0)]. Therefore, the composition based on strontium nitrate does not cause secondary damage to electronics/electrical equipments. Strontium salt based AFCs have lower fire extinguishing efficiency than Potassium salt based AFCs, this is because of high decomposition and high evaporation temperature of strontium salts [\[8](#page-27-0)]. Due to higher temperature requirements, strontium suffers in ease of aerosolisation and their participation in the homogenous fire suppression. To measure the suitability of CAFES in electrical equipment, electric insulation resistance is calculated. Calculation of insulation resistance of precipitant of fireextinguishing aerosol is carried out according to clause 10.2 of standard GB499.1- 2007 [[46\]](#page-29-0). Spaces having electrical and electronic units are associated with high level of fire hazard. This is due to the presence of energized equipment such as cables, which can be heated up to $200-300^{\circ}\text{C}$ and more due to short circuit conditions. Various experiments have been performed by Vladimir et. al, to establish effective ways of using condensed aerosols for fire suppression in electrical spaces [\[48](#page-29-0)].

Variety of strontium based salts has been used for the preparation of AFCs, Table [5](#page-8-0) [[40,](#page-28-0) [42](#page-28-0), [46](#page-29-0), [49–51\]](#page-29-0). Strontium salts have been used alone or in combination with other oxidizing agents. Strontium nitrate $(15-50\%, w/w)$ based compositions have been developed to achieve the fire extinguishing concentrations of 28– 200 mg/m^3 [\[40\]](#page-28-0). The application of magnesium based salts has also been emphasized to get water insoluble combustion by-products to reduce secondary damage [\[42](#page-28-0)]. Metaphosphate, nitrate, metasilicate and iodide of strontium $(30-47\% \text{W})$ along with carbonate, nitrate, bicarbonate and nitrite of potassium $(21-35\%, w/w)$ have been used as oxidizers [[46\]](#page-29-0). Reducing agent, binder and additives were taken in the percentage range of $10-25$, $2-10$ and $2-10$ respectively. AFC having strontium iodide (40%, w/w), potassium nitrite (30%, w/w), pentaminotetrazole (23%, w/w), epoxy resin (4%, w/w) and aluminium powder (3%, w/w) indicated the best electrical insulation resistance of $\geq 16 \Omega$.

Strontium nitrate (55–70%, w/w), dicyandiamide (3–8%, w/w), phenolformaldehyde resin (5–15%, w/w), hexamethylenetetramine (5–12%, w/w), carbon (5–12%, w/w) and potassium fericyanide (0–8%, w/w) based AFC has given the electrical insulation of $> 30 \Omega$ [[49\]](#page-29-0). Here, hexamethylenetetramine has been used as disinfection purification agent for nitrogen oxides. The only problem associated with the application of strontium based oxidizing agent is the reduction in fire extin-guishing efficiency [\[49](#page-29-0)]. The electric insulation increased up to 80 Ω using stron-tium permanganate (51%, w/w) based AFC [[50](#page-29-0)]. Attempts were further made to increase the electric insulation, $> 120 \Omega$ using strontium bromide (58%, w/w), barium nitrate (12%, w/w), guanidine nitrate (23%, w/w), PTFE (4%, w/w) and iron oxide $(3\%, w/w)$ based composition [[51\]](#page-29-0). Since guanidine nitrate has explosive nature, its application may bring safety issue. The working principal of strontium salts is similar to that of potassium based salts.

4.4. Other Oxidizing Agents

Apart from using potassium nitrate or/and strontium nitrate, other metal salts have also been explored to prepare AFCs, Table [6](#page-9-0) [\[40](#page-28-0), [42](#page-28-0), [52\]](#page-29-0). Magnesium nitrate has been considered as most useful oxidiser for preparations of AFCs [\[40,](#page-28-0) [42\]](#page-28-0). The application of magnesium based salts has been emphasized to get water insoluble combustion by-products to reduce secondary damage [\[42](#page-28-0)]. Compositions comprising of potassium perchlorate (40–50%, w/w), epoxy resin (9–12%, w/w), potassium chloride (40–44%, w/w) and magnesium powder (0–4%, w/w) have been prepared to achieve the fire extinguishing concentration of 80 g/m³ [[32\]](#page-28-0). Here, magnesium powder was used as burn rate modifier and potassium chloride to control the temperature of aerosols by absorbing some of the heat of the oxidation-reduction reactions.

Recent advancement in aerosol forming composites is the application of fire extinguishing chemicals viz., ferrocene [\[53](#page-29-0)], metallic oxy salt [[54\]](#page-29-0), transition metal compound [\[55](#page-29-0)] and heterocyclic compounds [[56\]](#page-29-0) with K-type or S-type AFCs. These fire extinguishing compositions utilizes pyrotechnic aerosol forming composites as a heat source or power source. The combustion of the pyrotechnic agent produces a large amount of heat, which is utilized to vaporize fire extinguishing substance, which is sprayed out together with the pyrotechnic agent aerosols. Such systems eliminate the requirement of cooling systems due to endothermic decomposition reaction of fire extinguishants, e.g., heterocyclic compounds.

5. Condensed Aerosol Based Fire Extinguishing System (CAFES)

Powder or granules of AFCs once prepared are moulded at specified pressures to prepare a block in desired shape and size. AFC blocks are attached to igniters and assembled within the casing of aerosol based fire fighting system (CAFES, Fig. [3\)](#page-20-0). The combustion of AFC can either be initiated manually or automatically using internal thermal or electrical ignition mechanisms. Cooling system (pallets/granules) is placed in the path of hot aerosols to bring their temperature down to acceptable limits. CAFES can also be attached to fire sensors to bring an independent auto actuation feature.

Modified CAFES systems with additional oxidizing agent and in path filtration systems have also been proposed [\[33](#page-28-0)]. Additional oxidizing agent system contains zeolites having surface adsorbed potassium nitrate. In real time, oxidiser decomposes due to the heat produced during combustion of AFC and produces oxygen. This in turn reacts with incompletely oxidized products, viz., CO, H_2 , NH₃ and CH₄; and converts them to CO_2 , H₂O, N₂ and CO_2 . Thus produced gases and aerosols are cooled through coolant (water saturated zeolite) or metal casings. Aerosol and gas mixtures are additionally chemically purified within the bed of filtering sorbent having aqueous potassium bicarbonate over zeolite. Various international standards such as, ISO 15779; international maritime organization-MSC/ Circ.1007, 26 June 200; Netherlands: BRL-K23001/03; Australia/New Zealand:

Figure 3. Internal view of condensed aerosol based fire extinguishing system.

4487:1997-AS/NZS 1851.16:1997; European Committee for Standardization: EN 15276-1 and 2; NFPA-2010; Underwriter Laboratory: UL-2775, etc. have been considered for test and evaluation of aerosol based fire fighting systems. The description of various standards has been provided as Table [6](#page-9-0). There are many manufacturers/suppliers, which supply aerosol based systems worldwide; Table [8.](#page-21-0)

6. Aerosol Generation and Fire Extinguishing Mechanism

AFC consists of an oxidizer, a reducer, a binder and several processing technological additives. Fire extinguishing mechanism of aerosol forming composition is give Fig. [4.](#page-21-0) These ingredients are grounded into fine powder, mixed in definite proportions and compressed to get AFC blocks. AFC blocks in CAFES are ignited using suitable ignition mechanism or due to self thermal ignition properties [\[57](#page-29-0)]. When the flame generated through electrical or thermal igniter, comes in contact with AFC, at the junction point the oxidizer decomposes and produces oxygen. Thus produced oxygen reacts with the fuel exothermally and initiates the combustion process, which produces solid particles (40%) and gases (60%) . Tech-

Table 8 World-Wide Manufacturers of Condensed Aerosol Based Fire Extinguishing System

Figure 4. Free radical based fire extinguishing mechanism of aerosol forming composition.

nological additives accelerate and stabilize the combustion process. Gas forming agents decompose at flame temperature and produce hot gases.

Until discharged, aerosol particles remain in vapour state, then cooled and condensed within the system, and finally discharged as solid particulates. Combustion products may include particles like metal oxides, carbonates, chlorides, etc. (where Metal = Na, K, Mg, Ca, Sr or Al); and gaseous products include N_2 , CO₂, CO₂, CO₂, C₀², C₀ $NH₃$, $H₂O$ and traces of hydrocarbons. With $KNO₃$ the reaction can be: $KNO_3 + \text{Reductant} = K_2CO_3 + \text{KHCO}_3 + \text{Gases}.$ The particulate matter (aerosols) floods to the fire zone due to the thrust of co-produced gases. Due to sub micron sizes, aerosol particles remain airborne significantly longer, and leave much less residue within the protected area. Condensed aerosols are flooding agents and, therefore, effective regardless of the location of the fire.

In order to extinguish the fire, one of the four factors (fuel, oxygen, heat and chain reaction) needs to be suppressed / removed. At the fire zone, the particulate matter, mainly composed of metal carbonate decomposes endothermically to produce metal oxide, which reacts with water to produce metal hydroxide. The latter decomposes in fire and generates metal radicals, which in turn react with hydrogen, oxygen and hydroxide radicals of fire sustaining chain reactions. These interactions break the chain reaction of fire and subsequently extinguish it. Whilst, the coproduced inert gases dilute the oxygen concentration to suffocating levels to the fire. Decomposition and vaporization of solid particles is endothermic, thus the process absorbs heat from the fire zone and subsequently cools it. Aerosol particles exhibit fire extinguishing by homogenous catalytic inhibition mechanism, similar to that of Halon.

$$
MOH + H^* = H_2O + M^* \tag{1}
$$

$$
M^* + OH^* = MOH \tag{2}
$$

$$
MOH + OH^* = H_2O + MO^* \tag{3}
$$

Moreover, the cloud of aerosol micro particles engulfs the flame and offers a sufficiently large combined surface area to absorb its heat. On the surface of these sub micron particles, recombination reactions of fire sustaining radicals takes place as energy is absorbed, and fire is extinguished.

$$
O^* + H^* = OH^* \tag{4}
$$

$$
H^* + OH^* = H_2O \tag{5}
$$

7. Advantages vis-a-vis Disadvantages and Related Toxicity Issues

Aerosol based fire fighting technology is one of the most leading, fast and reliable technology technologies in fire science. It has tremendous advantages over the conventional fire fighting technologies. One of the international supplier (M/s Pyrogen) has indicated that aerosol based systems occupy minimum area in comparison to other fire extinguishing agents/technologies, Fig. 5 [\[6](#page-27-0)]. Aerosol based system occupies 4 and 37 times less space than Halon 1301 and inert gases respectively. Since CAFES is an independent modular unit and does not require pressurized container, it offer the extended shelf-life, reduced container weight, minimized leakage and safety issues, reduced maintenance routines and requires less space. CAFES is approx. ten times more effective than the presently used Halon alterna-tives [[58\]](#page-29-0). CAFES can extinguish class A, B, C, D and K fires at 30 $g/m³$ to 200 g/m^3 design concentrations of AFC [\[8](#page-27-0)].

Although CAFES have found versatile fire fighting applications in almost all defence and civil areas, even it has few limitations or drawbacks. In general, AFC on ignition produce particulate matters (K_2CO_3) and KOH), inert gases/vapours $(CO₂, H₂O$ and N₂) and toxic gases (HCN, NH₃ and CO). CAFES generates fine particulate matters, which percolate to hidden spaces, settle with time and bring cleanliness issues. Aerosol particulates and gases absorb and scatter light, and bring reduction in visibility in the fire zone. Potassium nitrate based AFCs produce corrosive particles (KOH) and acidic gases (NOx and $CO₂$), which can damage delicate electronics and electrical equipment [[59\]](#page-29-0). KOH has little toxicity (up to 2.0%: irritation; $> 2.0\%$: corrosive, LD50: 273 mg/Kg for rat, recommended exposure limit: 2 mg/m^3). The problem of KOH can largely be solved by substituting alkaline metals with alkaline earth metals. Concerns have also been shown for possibilities of CAFES as latent ignition source for fuel-air vapour mixture due to heated system or high temperature of hot aerosols during fire fighting [[60\]](#page-29-0). Basically, the combustion temperature of AFC is mainly above 1200 K [[59\]](#page-29-0) such high temperature brings potential risks of secondary fire. In order to reduce the temperature of hot aerosols, coolants are installed within the housing of CAFES after AFC. Coolants are substances which undergo endothermic decomposition.

Figure 5. Space requirement for various fire extinguishing agents.

They absorb the heat released by AFC and hence decrease the temperature of aerosols.

AFC on combustion produces particulate matters of size $< 10 \mu$ and gases. The solid particulate aerosols have a considerably smaller mass median aerodynamic diameter (MMAD) than those of dry chemical suppression agents $(25-150 \mu)$. Micron size aerosol particles can cause adverse health effects once inhaled. These particles can deposit on the bronchi walls and bring chronic or acute respiratory diseases [\[61](#page-29-0)]. Micron size particles cause irritation of the mucous membranes and invade the blood vessels without practically being evacuated from the body. Co produced toxic gases, viz., NOx, CO, NH₃, HCN $[62]$ $[62]$ and hydrocarbons also cause health problems [\[59\]](#page-29-0).

Valeriy et al [\[30](#page-28-0)] evaluated the toxic effect of CAFES on white mice. The subjects were exposed for a period of 15 min to a concentration of 60 $g/m³$ and monitored for a period of 2 weeks. The best aerosol forming composition with 10% each of dicyandiamide and potassium bicarbonate showed no observed toxicity from exposed mice under the conditions of test. Dicyandiamide produced toxic effects and lower fire extinguishing performance, if taken $\geq 25\%$. To counter the toxicity issues, strict regulations have been made in countries like U.S., Russia, Australia and China to limit the maximum concentration of hazardous gases released by condensed aerosol forming agent. Because of the toxicity issues, US EPA has approved CAFES for non-occupied or not normally occupied areas [\[9](#page-27-0)] Some of the countries like Russia, U.S., Australia and China have already developed standards and norms for manufacturing and quality control of AFC and CAFES for different fire protection scenarios.

The formation of toxic gases can be controlled either by selecting the appropriate aerosol forming composition or arranging gas absorption/neutralization systems within the path of aerosols before being discharged. Cooling pallet composition can also incorporate the toxic gas neutralizing chemicals to minimize the toxic gases. Highly porous zeolites, such as activated aluminium oxide (surface area, 300–345 m²/g) with copper can be used as catalytically active substance to reduce the toxic gases [\[32](#page-28-0)]. At higher temperature ($> 800^{\circ}$ C), oscillations of zeolite lattice increases, which in turn facilitates the penetrations of molecules to absorption sites resulting catalytic neutralization reactions and complete oxidation.

8. Real Time Applications

Condensed Aerosol based fire extinguishing systems have found a large number of applications in various fields such as marine, telecommunications, warehouses, etc, as provided in Fig. [6](#page-25-0). CAFES have used promisingly in transportation, domestics, offices, public places, industries, machinery, electronics, electrical, telecom, warehouse, marine, and military areas. It can be used as an independent fixed, mobile, hand held and grenade device. A report on options of Halon for aircraft applications has indicated that the aerosol based fire fighting systems may be used as total flooding system [\[9](#page-27-0)]. CAFES systems with qualified military standards are

Figure 6. Real time application areas of condensed aerosol based fire extinguishing system.

currently protecting the engine compartment of more than 8000 US Army mine resistant, ambush protected vehicles. NASA has also selected CAFES as the fire suppression system for its giant twin crawler transporters.

Due to high temperature of aerosols, its application for combustible and explosive materials facilities is difficult. But one of the ways of making it safe for such critical applications is to distribute the aerosol to protected enclosures by means of piping work [[63\]](#page-29-0). This reduces the temperature of aerosol and at the same time allows arranging one set of CAFES to protect several enclosures simultaneously. To reduce the effect of piping, aerosols can be forwarded using inert gas system in conjugation with the CAFES. This type of arrangements can also find various applications, where fire fighting media can be launched from a distance. Moreover, the aerosol based fire fighting technology has not been widely utilized but its simplicity and effectiveness attracts widespread applications.

9. Conclusion and Future Prospects

Potassium nitrate has been widely considered as the most popular oxidizing agent for aerosol based fire fighting compositions. This is because of its, readily availability, reasonable cost, low hygroscopicity and ease of ignition of mixtures containing it. Among the different compositions, AFCs having potassium nitrate (40– 75%, w/w) as oxidiser, phenolformaldehyde resin $(10-15\%$, w/w) as fuel cum binder, guanidine nitrate (10–15%, w/w) as supplementary fuel cum gas forming agent and transition metal salts $(2-5\% \text{W})$ as burn rate modifier appeared to be most promising, however, the choice depends on application. Strontium nitrate based compositions are less efficient than potassium nitrate based compositions, but these can be safely explored for fire extinguishing of electrical and electronic systems as it prevents corrosion and maintain their insulation resistance. AFCs were found approximately four times more effective than the presently used Halons per unit mass. AFCs indicated the burn rate in the range of 2–7 mm/s and fire extinguishing concentration as low as 8.0 g/m^3 . Moreover, AFCs could extinguish A, B, C, D and K classes of fire at a design concentration up to 200 $g/m³$. Variety of AFCs has shown no observed toxicity under the conditions of test. Moreover, AFCs are space effective, cost effective and environmentally safe (negligible GWP, ODP and ALT). Furthermore, the development of highly efficient, non-corrosive, non-toxic and environmentally benign aerosol forming compositions is still required and can be taken up by research groups.

CAFES leaves a little residue after application; hence, a cleanup procedure needs to be followed subsequent applications. Despite of these limitations CAFES has other benefits over currently used fire fighting technologies/systems. In comparison to gaseous systems, which operate at high pressure CAFES functions at low pressure, hence, attracts wider application domain. Overall, aerosol based fire fighting technology is a leading, fast and reliable technology for critical fire extinguishing applications. CAFES have found variety of applications in transportation, domestics, offices, public places, industrial, and military areas. Further research must be focused to improve its several properties such as: fire extinguishing efficiency, burn rates, storage life, toxicity of combustion products, minimum fire extinguishing concentration, fire extinguishing time, etc. Efforts can be made towards greening (with environmental friendly ingredients) the AFCs. Moreover, the technology has not been extensively utilized but its simplicity and effectiveness attracts widespread future applications, which needs to be explored.

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