Thermal and Chemical Degradation of Portland Cement Concrete in the Military Airbase

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Abstract: The military airbase especially aprons and the rigid pavement are often exposed to engine oil, hydraulic fluid, Jet oil, extreme heat shocks, and varied lengths of repetitive cyclic heat loading. Oils spillage during maintenance of aircraft on the parking apron or venting of oil from the aircraft after the main engine starting is a common phenomenon and inevitable in the airbase. Considering this, the paper presents the degrading mechanism of ordinary Portland cement (OPC) and Portland limestone cement (PLC) concrete in the parking apron and rigid pavement of military airbase. This study identifies the potentially damaging compounds (hydrocarbons) likely present on the airbase. The chemical reactions between Portland cement and the hydrocarbons and their consequences in the airbase concrete are also presented in the study. The effect of auxiliary power units (APUs) exhaust temperature on the airbase concrete and the combined effect of heat and spilled chemical is explained in the present study. The study reveals that APUs exhaust temperature is sufficient enough to develop thermal cracks in the concrete, as a result, the permeability of concrete increases that allows more chemical spillage in the concrete. The spilled hydrocarbons react greatly with the Portland cement and produce soft salty brittle materials on the top cementitious layer of OPC and PLC concrete that is known as scale. The APUs exhaust temperature accelerates the pace of chemical reaction and the surface degradation process of OPC and PLC concrete in the military airbase.

Keywords: Airbase, jet exhaust, chemical damage, high temperature, scaling

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1 Introduction

Ordinary Portland cement (OPC) is the most common type of cement for general use in civil engineering construction around the world from the mid-19th century. The OPC is produced from the hydraulic lime and usually originates from limestone. Due to widespread availability and low cost of the limestone, the production cost of OPC is reasonably low. Consequently, the OPC was widely used in the construction of aprons and rigid pavements of the military airbase to support the fighter aircraft. Moreover, Portland limestone cement (PLC) is also widely used around the world. The addition of limestone in the Portland cement has some technical, environmental and economic benefits. It reduces the global carbon dioxide emission, increases the strength of cement and saves the energy. PLC has been used in Europe for over decades. Canadian Standards Association (CSA) has allowed the incorporation of limestone in Portland cement since 1983 [1]. Recently, America, Australia, China, India and other some countries around the world is also using limestone as mineral additives in the Portland cement.

The airbase apron and rigid pavement concrete surfaces are regularly exposed to extremely severe circumstances not often experienced by other concrete surfaces. In addition to the expected dynamic loads, these pavements are often exposed to engine oil, hydraulic fluid, jet fuel, extreme heat shocks, and varied lengths of repetitive cyclic heat loading. McVay et al. reported that both the United States Air Force and Navy have been experiencing concrete scaling on their B-1 and F/A-18 parking aprons [2-4]. Moreover, military airbases in Australia also have been experiencing concrete scaling for over three decades, since the F/A-18 was purchased and placed into service in 1984 [5]. Usually, such concrete damage takes place in the form of scaling, or else it peels off from the wearing surfaces, is a regular occurrence in the airbase. This scaling is arisen within the first six to eighteen months because of cyclic running and maintenance of aircraft on the concrete [2]. Further, scaling develops progressively at a shallow depth of 6mm to 13mm beneath the top surface of concrete [2, 6]. However, the Department of the Air Force of USA has stated in their engineering technical letters that scaling damage occurs on the top 25 to 50mm of the rigid pavement [7]. This scaling can generate a significant amount of foreign object debris (FOD) in the form of released aggregate and poses a significant threat to the safety of both aircraft and personnel. FOD of any quantity is not tolerated in military airfields, as if a single piece of loose aggregate enter into a jet engine, it might be exploded, which can cause hundreds of thousands of dollars of damage with potential loss of human life of limb [8]. As reported in airfield pavement maintenance manual of the Royal Australian Air Force (RAAF) any scaling event to be rectified and states that scaling alone can classify the pavement as failed and be a severe hindrance to the safe operation of aircraft [9].

OPC lost 55% of its compressive strength after 7 days of continuous exposure to engine oil and water at high temperature [3]. Further, the Portland cement binder should be replaced by a neutral pH cement binder in the case of military airbase construction [4]. Most of the published papers concluded that the airbase concrete is subjected to surface scaling due to its high pH value [2-4, 6]. Moreover, McVay et al. identified that ester presence in both engine oil and hydraulic oil reacts with the calcium hydroxides present in OPC concrete and produces calcium salt and alcohol [2]. This calcium salt of the fatty acids are soft, slightly soluble in water and known as scale on the top surface of the concrete. However, the actual process of chemical and thermal degrading mechanisms and military airbase circumstances are still left unanswered.

The purposes of this paper are to identify the damaging chemical compounds that are likely present in the military airbase, the actual process of chemical degradation of OPC and PLC concrete as well as to re-evaluate the thermal degradation of military airbase concrete. In the light of this, the paper presents the chemical reactions and chemical degradation process when military airbase parking aprons are exposed to ester based synthetic hydrocarbons under the exhaust gas temperature of auxiliary power units (APUs) of modern combat aircraft such as F/A-18s, B-1s, V-22 Ospreys. Further, the paper presents the actual military airfield conditions those are responsible and affect the durability of concrete.

2 Military Airfield Circumstances

Oils spillage during maintenance of aircraft on the parking apron or venting of oil from the old aircraft after the main engine starting is a common phenomenon and inevitable in the airbase.

Usually, the military airbase is exposed to by the three primary hydrocarbons, such as engine oil (MIL-PRF-23699 or MIL-L-7808), jet fuel (F-34 or similar), and hydraulic oil (MIL-PRF-83282). Engine oils are saturated ester based lubricants. Jet fuel is almost hundred percent kerosene, and hydraulic oil is the synthetic hydrocarbon-based on phosphate-esters and is hygroscopic [10]. The chemical breakdown of the potentially damaging compounds of those oils is presented in Table 1.

Table 1 Breakdown of hydrocarbons likely present on airbase

Fluid name	Military designation	Potentially damaging compounds	Concentration %
Engine oil	MIL-PRF-23699	Fatty acids, C5-9, tetraesters with pentaerythritol	≥70 - ≤90
		Fatty acids, C5-9, hexaesters with dipentaerythritol	≥5 - ≤10
		tris(methylphenyl) phosphate	<5
		Benzenamine, N-phenyl-, reaction products with 2,4,4-trimethylpentene	<5
Jet fuel	F-34/AVTUR/ FSI	Kerosene (petroleum), hydrodesulphurised	0-100
		Kerosene	0-100
		Diethylene glycol monomethyl ether	0-0.15
Hydraulic oil	MIL-PRF-83282	1-Decene, tetramer, mixed with 1-decene trimer, hydrogenated	≥60 - ≤100
		2,2',6,6'-tetra-tert-butyl-4,4'-methylenediphenol	<10
		Distillates (petroleum), hydrotreated heavy paraffinic	<10
		Phenol, isobutylenated, phosphate (3:1) [Triphenyl phosphate > 25%]	<10

Furthermore, the airbase concrete surfaces are often saturated by the rainwater and sometimes the water table is found at the surface level of concrete. In addition to that, the military airbase is subjected to thermal cycle by the APUs exhaust of aircraft. McVay et al. reported that the surface temperature of airbase concrete is about 175 °C when it is subjected to APUs exhaust for both F/A-18 and B-1 aircraft [3]. APUs exert the exhaust on the military airbase concrete at radial nature and the maximum surface temperature of concrete at the centre of the footprint is 177°C with a velocity of 229 km/h [11]. Figure 1 indicates the surface temperature of concrete at the APUs impingement zone.

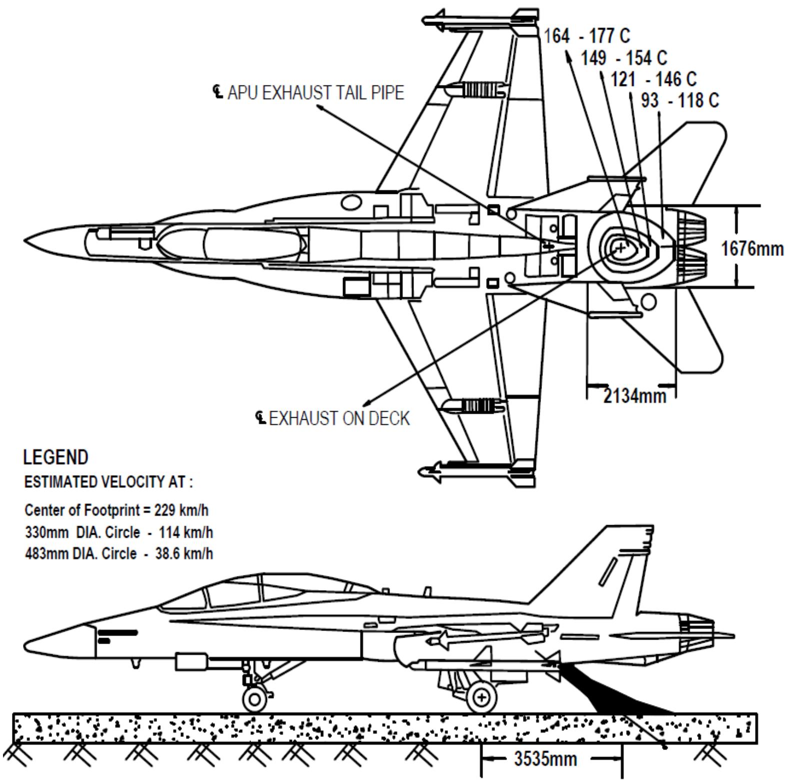

Figure 1. The surface temperature of concrete at the APUs impingement zone [11].

Moreover, Duane also has stated that the maximum surface temperature of airbase concrete is 175 °C and the heating rate is over 3 °C/sec in the first 15 seconds and approximately 70 °C/min in the first minute when subjected to APUs exhaust of F/A-18 [5]. The surface heating profile of airbase concrete is shown in Figure 2. Interestingly the maximum temperature of pavement was only reached after the APU went into an overdrive mode during the shutdown sequence, which can be seen in Figure 2 as the peak near the end of the recorded data. Furthermore, Figure 3 shows the hydrocarbons are floating on the run-off water on an apron of the airbase.

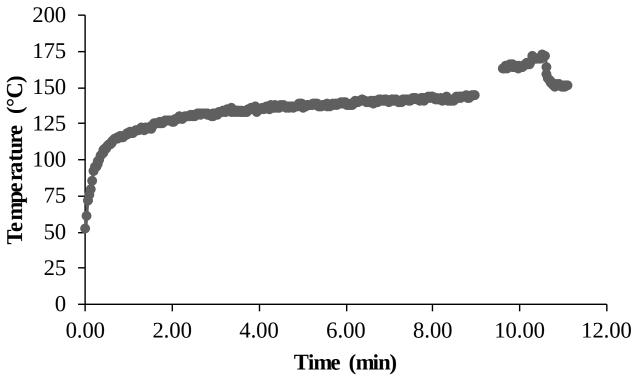

Figure 2. The surface temperature profile of airbase concrete when exposed to the F/A-18 APUs exhaust [5].

Figure 3. Oils are floating on the run-off water on an apron

3 OPC and PLC Concrete

Both the Portland cement clinker and limestone contain a large percent of calcium oxide (CaO). Table 2 presents the typical chemical composition of clinker and limestone. When calcium oxide comes into contact with water it produces calcium hydroxide. Equation 1 shows the hydration of calcium oxide.

$$CaO\ (s) +\ H_2O(l) \rightarrow\ Ca(OH)_2(s) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

The calcium hydroxide, $Ca(OH)_2$ is traditionally known as slaked lime, has a pH value of 12.20, and this strong alkaline material can react with most of the acids. Normally, the percent of solid calcium hydroxide is 20 to 25 in hardened cement paste. Furthermore, the unreacted clinker and limestone powder also might be exist in the hardened concrete.

According to the European pre-standard prEN 197-1, the limestone content in type II/A-L and type II/B-L cement are 6–20% and 21–35%, respectively, with the primary requirement is $CaCO_3$ content in the limestone must be greater than 75% [12]. Further, it is believed that the future use of PLC around the world will be increased significantly [13].

Table 2 The typical chemical composition of clinker and limestone

Composition (%)	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	SO_3	LOI
Clinker	21.79	5.13	3.59	66.42	1.71	0.55	0.09	0.52	1.5
Limestone	0.61	0.15	0.17	53.36	1.47	0.02	0.00	-	43.54

4 Degradation of Military Airbase Concrete

4.1 Chemical degradation

Engine oil contains fatty acids, C5-9, tetraesters with pentaerythritol up to 90% and fatty acids, C5-9, hexaesters with dipentaerythritol up to 10%. Similarly, McVay et al. stated that the ester content in the lubricating oil and hydraulic oil are 95% and 30%, respectively [3]. This ester is soluble in normal water in presence of heat. When these esters come into contact with water in presence of heat, it hydrolyses to carboxylic acid and alcohol. The equation 2 explains the hydrolysis of the ester.

$$CH_3COOR'(ester) + H_2O \xrightarrow{heat} CH_3COOH(\text{carboxylic acid}) + R'OH \ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

Typically, the carboxylic acid is colourless liquid with very strong odours (pungent smell) and this acid is a weak acid having a pH of around 2 to 6. Despite being a weak acid, carboxylic acid behaves like any other acid and can react with soluble and insoluble alkalis and carbonate to form salts and water. The equation (3) and (4) present how the carboxylic acid reacts with alkali and carbonate.

$$CH_3COOH + Ca(OH)_2(calcium\ hydroxide) \rightarrow Ca(CH_3COO)_2\ (calcium\ salt) + H_2O \ldots (3)$$

The carboxylic acid reacts with calcium hydroxide presents in OPC and PLC concrete produces calcium salt and water. Additionally, Carboxylic acid also can react with calcium carbonate present in PLC produces calcium salts, water, and carbon dioxide.

$$CH_3COOH + CaCO_3(calcium\ carbonate) \rightarrow Ca(CH_3COO)_2(calcium\ salt) + H_2O + CO_2 .. (4)$$

These calcium salts of fatty acid are soft, soapy materials that have the rancid odour, which supports the physical properties of damaged samples collected by the US Air force [2]. Thus, the produced calcium salts in both equations are known as scale in the military airbase. Moreover, the pace of reaction depends on the temperature and pH value of cement. Since OPC and PLC both have a pH value greater than 12, and APUs exhaust makes the surface temperature of concrete around 175 °C, therefore, this reaction happens at a very faster rate on the top cementitious layer of concrete.

Both the engine oil and hydraulic oil containing phosphate esters in the form of tris(methylphenyl) phosphate and triphenyl phosphate. These compounds help to lubricate steel and reduce wear due to heat and friction. The triphenyl phosphate is a colourless ester (triester) of phosphoric acid and phenol. It is used as a flame retardant and plasticizer in hydraulic fluids. Triphenyl phosphate is biodegradable under anaerobic conditions and soluble in water [14, 15].These phosphate esters present in both the engine oil and hydraulic oil can be formed in phosphoric acid when it comes into contact with water at high temperature [16]. Equation (5) illustrates how phosphoric acid can be formed from phosphate ester.

$$C_{18}H_{15}PO_4\ (phosphate\ ester) + H_2O \xrightarrow{T\approx150-220°C} C_{18}H_{15}PO_4\ (unreacted\ fluid) + H_3PO_4\ (phosphoric\ acid) + C_{18}H_{15}OH \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots .(5)$$

In addition to that, a small percent of red phosphorus is also added to the engine oil to act as a scavenger for oxygen and water. The red phosphorus can be oxidised simply in the air and produces phosphorus pentoxide. Equation (6) shows the production of phosphorus pentoxide.

$$P\ (\text{red phosphorus}) + O_2 \rightarrow P_2O_5\ (\text{phosphorus pentoxide}) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (6)$$

The phosphorus pentoxide reacts with water, even though it can react with the moisture in the air, to form phosphoric acid. Equation (7) presents the production of phosphoric acid from phosphorus pentoxide.

$$P_2O_5 + H_2O \rightarrow H_3PO_4\ (\text{phosphoric acid}) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (7)$$

These phosphoric acids produced from phosphate ester and red phosphorus can react with the calcium hydroxide presents in OPC concrete and react with calcium carbonate present in PLC concrete. Equation (8) and (9) show the reaction between phosphoric acid and calcium hydroxide and reaction with calcium carbonate, respectively.

$H_3PO_4 + Ca(OH)_2 \rightarrow Ca_3(PO_4)_2$ (calcium phosphate) $+ H_2O$ … … … … … … … … (8)

$H_3PO_4 + CaCO_3 \rightarrow Ca_3(PO_4)_2$ (calcium phosphate) $+ CO_2 + H_2O$ … … … … … … … (9)

The phosphate esters and the red phosphorus could be decomposed in water and air oxidation in presence of heat and produces phosphoric acid. These phosphoric acids can attack the OPC and PLC concrete and produces calcium phosphate in the top cementitious layer, resulting in a soft, spongy material also known as scale. In summary, when the scale is being developed in the top cementitious layer of concrete, the top layer of concrete becomes more brittle and reduces the elasticity of concrete. As a result, aggregates or plate-like pieces peel off from the top layer of the concrete due to mechanical abrasion that contributes a significant amount of FOD in the military airbase. Figure 4 shows the effect of scaling on an airbase apron.

Figure 4 Aggregates are peeled off from the top layer of the concrete on an airbase apron.

4.2 Thermal degradation

The peak temperature and the rate of heating have a major influence on the thermal degradation process of OPC and PLC concrete. When that concrete is exposed to APUs exhaust temperature, the free water evaporates in the range of 30 -105 °C, gypsum and ettringite are decomposed in the range of 110 -170 °C and the C-S-H gel dehydration occurs at 180 °C [17]. Moreover, Portland cement concrete starts to lose its chemically bonded water at around 121 °C and the highest rate of dehydration occurs at around 177 °C [18]. Further, Hager argues that the structure of Portland cement paste damages partially due to dehydration at a temperature of 105 °C [19].

Often vapour pressures in the pore of saturated concrete are detrimental eventually be sufficient to cause tensile cracks in Portland cement concrete because concrete temperature beneath an F/A-18 reaches 140 °C in about 2 minutes. Furthermore, when gypsum and beneficial crystal ettringite are decomposed, sulphate reacts with aluminum and calcium and start to expand the volume of mass. As a result, micro-cracks are developed around the aggregate that decreases the elasticity and increases the permeability of concrete. Finally, If the chemically bound water is started evaporating, the strength of concrete decreases exponentially because 50% of cement paste strength is contributed by the cohesive force of C-S-H gel.

The aggregates in the concrete also play a vital role in the thermal degradation of concrete at high temperature. When concrete is exposed to high temperature, the volume of aggregates also expands according to the thermal expansion coefficient of aggregate used. Higher the thermal expansion coefficient of aggregate higher the expansion of the volume of concrete because generally, the aggregate is more than 70% in concrete. Consequently, tensile stresses are developed around the aggregates that also produces micro-cracks in the concrete. Ultimately, more penetration of oils and water in the upper layer of concrete and faster the surface degradation process.

4.3 Combined effect of thermal and chemical

Travis & Mobasher explained that heat causes micro-cracking in the concrete that directly increases the permeability and decreases the elastic modulus of concrete [20]. The increased permeability would allow more hydrocarbons to penetrate the concrete and increase both the surface and interface area between the concrete and the damaging compounds present in engine oil, hydraulic oil, and Jet fuel. Therefore, when hydrocarbons come into contact repeatedly with the cement paste and unsaturated dust of OPC and PLC concrete under the cyclic APUs exhaust heat, the chemical degradation of airbase concrete take place on a larger scale at a faster pace.

5 Probable Solution

McVay et al. [2] proposed neutral pH cement that is aluminum and/or magnesium phosphate cement, Hironaka & Malvar [6] recommended the magnesium ammonium phosphate cement for the military airbase concrete. In the study, the authors suggest geopolymer concrete and/or polymer-modified concrete containing heat resistant aggregates such as expanded shale, expanded slate, basalt, and limestone as coarse aggregate for military airbase repairing and construction. The geopolymer concrete has superior acid resistance [21, 22], spalling resistance and heat-resisting capacity than OPC due to their low differential gradients and thermal incompatibility between the geopolymer paste and aggregates [23]. Moreover, Polymer-modified concrete has low pH value, higher flexural strength and has a greater resistance to acid and base at elevated temperature [24]. In summary, the military airbase concrete should be made of high-strength concrete containing heat resistance aggregates and must have a lower permeability because lower permeable concrete has a greater resistance to chemical interactions.

6 Conclusion

APUs exhaust heat is sufficient enough to cause micro-cracks in OPC and PLC concrete at the military airbase, resulting in an increase of permeability and decrease of elasticity of concrete; consequently, more hydrocarbons have penetrated the interface of concrete. The APUs exhaust heat helps to hydrolyse the spilled chemical compounds and accelerates the pace of chemical reactions between cement and chemicals.

Both the engine oil and hydraulic oil contain a large amount of ester of fatty acid. These esters of fatty acid hydrolyse to carboxylic acid and alcohol. The carboxylic acid reacts with calcium hydroxide presents in OPC and calcium carbonate presence in PLC concrete, produces calcium salt and water at the top cementitious layer of concrete. These calcium salts of fatty acid are soft, soapy materials that have the rancid odour, are known as scale in the military airbase. Both the engine oil and hydraulic oil also containing phosphate esters and a small percent of red phosphorus. These phosphate esters and red phosphorus could be decomposed in water and air in presence of heat and produces phosphoric acid. These phosphoric acids can attack the OPC and PLC concrete and produces calcium phosphate in the top cementitious layer, resulting in a soft, spongy material also known as scale. When the scale is being developed, the top layer of concrete becomes more brittle and reduces the elasticity of concrete. As a result, aggregates or plate-like pieces peel off from the top layer of the concrete due to mechanical abrasion that contributes a significant amount of FOD in the military airbase. Therefore, the authors suggest geo-polymer concrete and polymer-modified concrete with heat resistant aggregates such as expanded shale, expanded slate, basalt, and limestone as coarse aggregate for military airbase repairing and construction.

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