

Damage to Aircraft Parking Ramps from Jet Oils and Auxiliary Power Units

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The precise cause for concrete damage observed in the vicinity of parked B-1 and F/A-18 aircraft has been determined. The combination of downward-directed auxiliary power unit (APU) blast and spilled aircraft oils are responsible for the scaling observed at these sites. Laboratory tests confirmed that ester-based lubricating oils and hydraulic fluids are chemically reacting with the hydroxyl component from the calcium hydroxide or the calcium silicate hydrate in the concrete and destroying the bond. The cyclic heating of the pavement by the APU greatly accelerates the reaction and facilitates the mixing and refluxing of aircraft fluids with the aqueous calcium hydroxide present. Laboratory techniques are demonstrated that duplicate the chemical reactions occurring in the field and allow for quick and accurate assessment of new materials before field testing. In addition, hydrolysis of lubricating oils and hydraulic fluids was replicated in a controlled laboratory experiment within 5 weeks, eroding a 10-cm (4-in.) concrete slab that was kept partially submerged in water.

Jet exhaust damage to concrete is not new, and it manifests itself in more than one form. For two decades, the F-4 aircraft eroded engine run-up pavements around the world. Today, the vectored thrust of the next generation of Harrier aircraft can spall a durable concrete surface in seconds. However, direct blast from the main engines of jet aircraft is not the only cause of surface damage. During the 1980s, the United States Air Force, Navy, and Marine Corps began to experience concrete scaling that was quite different from past erosion and spalling. This more recent damage, which is found on B-1 and F/A-18 parking aprons, is evident in parking areas on which auxiliary power units (APUs) impinge upon oil-soaked surfaces. This research has uncovered evidence that decisively separates the causes of concrete damage under vectored thrust from that related to aircraft APUs.

APUs

APUs were developed to provide aircraft generation support without having to use cumbersome ground equipment or run the main engines. They provide power for all electrical and hydraulic systems when the aircraft is parked and they can be used to start the main engines.

APUs are small turbojet engines with jet pipe exhaust temperatures of approximately 550°C (1,000°F) and exit velocities of about 135 m/sec (440 ft/sec). The exhausts of the B-1 and F/A-18 come out the bottom of the aircraft approximately 1.5

m (60 in.) and 1.0 m (40 in.) above the pavement, respectively, with angles of incidence of 45 degrees to the ground plane. Navy reports show the single exposure of an APU to be as long as 45 min, but 5 min is typical (1). APUs on the B-1, however, commonly run for 1 hr or more. Both the Navy and the Air Force have reported surface temperatures above 175°C (350°F) with exhaust velocities of more than 62 m/sec (203 ft/sec) at the pavement surface during APU operations. The location of the APU on an aircraft is normally one of the last design considerations. However, pavement damage and the potential for foreign object damage to jet engines have given more attention to APU placement on future aircraft.

SURFACE SCALING UNDER APUs

Each F/A-18 and B-1 aircraft is assigned a parking space on the apron, from which it seldom deviates. Aircraft maintenance is performed on the aircraft while it is sitting on the parking ramp. The scaling is found in areas of APU blast impingement where large amounts of spilled lubricants, hydraulic fluids, and jet fuels have been either vented by the aircraft or spilled during routine maintenance.

In the past, the Navy often rearranged aircraft parking layouts to reduce the potential for foreign object damage to the aircraft. And the Navy and Air Force have experimented with heat-resistant diabase aggregate, refractory concrete, and surface coatings (2). All have resulted in less than a year of service life. Steel plates bolted to the pavement at impingement locations are being used successfully by the Navy and the Air Force. After 4 years of service, the plates have prevented concrete scaling; however, they pose several operational safety problems and are considered to be only a temporary solution.

OBJECTIVE AND SCOPE OF WORK

The objective of this research is to identify the source of scaling under aircraft and propose a solution. Investigators from the Operability and Repair Branch of the Air Force Civil Engineering Support Agency (AFCEA) traveled from Tyndall Air Force Base near Panama City, Florida, to several bases to see the damage and collect concrete samples. Subsequent laboratory work concentrated on (a) reproducing the field damage under controlled conditions, (b) performing chemical analysis on field samples to assess the material alteration and its significance, (c) developing a laboratory test that can screen potential repair materials before field testing,

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and (d) offering recommendations to mitigate or eliminate this type of concrete damage.

FIELD INVESTIGATION

Researchers visited Cecil Field (F/A-18), Beaufort Marine Corps Air Station (F/A-18), and McConnell Air Force Base (B-1) in June and July 1991 to survey the damage and collect samples. The damaged concrete pavements at Cecil were made from granite, diabase, or soft limerock coarse aggregate, depending on the location on the airfield, and quartz sand. The Beaufort aprons were of granite or tough limestone aggregate and quartz sand. The McConnell concrete contained limestone aggregate. Inspection revealed that the zone of damage was confined to the APU impingement area in the presence of large spills of hydraulic fluid and lubricating oils.

Figure 1 is typical of the scaled concrete surface; the steel plate in the foreground is one of scores placed at Cecil Field to temporarily prevent further damage. Figure 2 is a close-up of a scaled piece of concrete that was easily flipped with fingertips. Initially, because of large amounts of exposed ag-



FIGURE 1 Concrete damage related to APU.

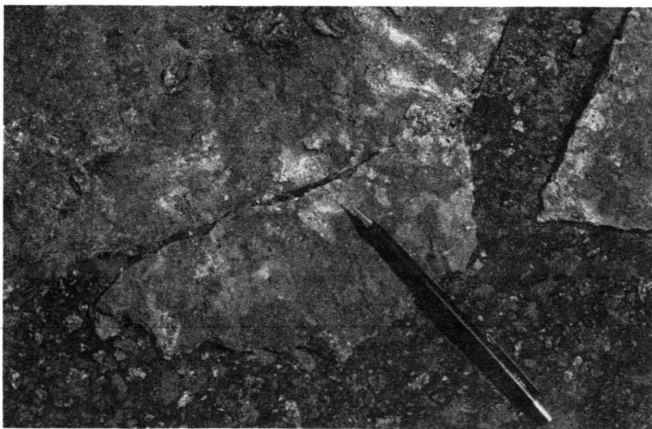


FIGURE 2 Scaling typical in older pavements.

gregate, it appeared the concrete aprons were delaminating at the paste-aggregate interface (Figure 3). However, the size of the scale and the entrapment of aggregate in scalings such as this suggested that the problem was not related to surface finishing. Full-depth cores 15 cm (6 in.) in diameter and 38 cm (15 in.) long were taken from the damaged areas; these cores revealed lubricant penetration from 1 to 2 cm (0.40 to 0.75 in.). Cores taken outside the zone of APU impingement, but within the fluid spill area, showed no surface damage and less oil penetration.

LABORATORY RESULTS

Slab Testing

Work was initiated at AFCESA to reproduce the field damage under controlled laboratory conditions. This entailed cyclic heating of two 1-year-old concrete slabs that were 0.92 m (3 ft) in diameter and 10 cm (4 in.) thick. Concrete aggregates were crushed limestone and silica sand. The heat source was a radiant heater with a 15.2-cm (6-in.) ceramic core controlled by a thermocouple attached to the center of the heated area. The heater cycled temperatures on the concrete surface to 162°C (350°F) for up to 2 hr, allowing at least 1 hr of cooling time between cycles. Two or three cycles per day, excluding weekends, were completed. One slab was continuously coated with hydraulic and lubricating fluids, and the other was not treated with oils. Both slabs were kept submerged in water throughout the 25-day period, except for the top 2.5 cm (1 in.), to simulate availability of water in the field.

Initially, fines appeared on the surface of the slab treated with the hydraulic and lubricating fluids. After 5 weeks of cyclic heating, 10-mm ($\frac{3}{8}$ -in.) aggregate started breaking loose from the surface. The damage was more like surface erosion than the scaling found in the field. There was no erosion observed in the slab that was not exposed to oils.

Chemical Investigative Tools Used

Because the scalings from the specimens were friable and rancid-smelling, they were considered to have been chemi-



FIGURE 3 Delamination of concrete below carbonated surface.

cally altered. These scalings were different from the spalled concrete resulting from jet blast, which is stronger and exhibits no material alteration.

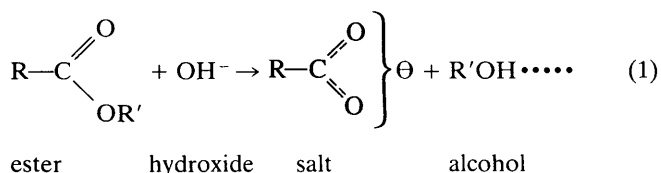
Consequently, a chemical study of the damaged concrete was initiated at both AFCESA and the Materials Directorate of Wright Laboratory (3). This entailed gas chromatography/mass spectroscopy (GC/MS) and scanning electron microscopy (SEM) with energy dispersive analysis X-ray at AFCESA; and GC/MS, infrared spectral analysis (IR), and X-ray diffraction (XRD) at Wright Laboratory. It was conjectured that the esters in lubricating oils (MIL-L-7808 and MIL-L-23699) and hydraulic fluids (MIL-H-83282) could have been hydrolyzing. Of the two major constituents of the spilled fluids—hydrocarbons and esters—only esters have been known to be detrimental to concrete (4).

Hydrolysis of Oils

Esters, which are chemically combined acids and alcohols, will break down (hydrolyze) when heated in an aqueous acid or base solution (5). Discussions with Hatco, a major manufacturer of raw materials in lube oils and hydraulic fluids, reveal that lubricating oils are composed of 90 to 95 percent ester blends and that hydraulic fluids are 30 to 40 percent esters.

If the oils or hydraulic fluids were undergoing hydrolysis, it would have to be of an alkaline variety, since the pH of concrete may be as high as 12. This is due to the strong base calcium hydroxide [$\text{CA}(\text{OH})_2$, pH = 12.4], which exists in both solution and crystal form in hardened portland cement concrete (6,p.867). Large and extensive crystals have been reported in young concrete in which 25 percent of the paste is calcium hydroxide (7). This is also true in very old cement paste (8). It has been reported that, for some aggregate types, calcium hydroxide provides both the bond as well as the load transfer mechanism between the aggregate and the cement mortar (calcium silicate hydrate) (9).

The reaction (5),



under alkaline conditions, produces the salt of the carboxylic acid and liberates the alcohol. In this reaction, the calcium hydroxide provides the (OH^-) anion, and the calcium (Ca^{2+}) cation is used in the formation of the acid salt. Believing this reaction to have caused the scaling observed, researchers set out to identify the products found on the scalings.

Identifying Reaction Products in Field Samples

At AFCESA, samples of the damaged concrete were crushed and mixed with an aqueous solution of sodium chloride and filtered. (Calcium salts of the fatty acids are slightly soluble in water, a polar medium, and insoluble in hexane, a nonpolar

solvent; whereas acids are soluble in hexane but not in water). The filtered wash was then split into two portions with one portion being mixed with hexane, which was subsequently extracted and injected into the GC/MS. This ensured that the aqueous sodium chloride wash did not contain any hydraulic fluids or lubricating oils. The second portion of the sodium chloride wash was mixed with concentrated hydrochloric acid, which would convert any salts present into their fatty (carboxylic) acid counterparts. Hexane was added, the whole mixture was shaken, and the hexane was extracted and injected into the GC/MS. Comparing the resulting mass spectra to library values revealed the presence of hexanoic, octanoic, and nonanoic acids, components of esters found in turboshaft oil. It was then deduced that the salts that produced these acids were residua from spilled turboshaft oil.

Using IR spectrum, Wright Materials Laboratory found that the lubricating oils and hydraulic fluids were absent in the surface scalings but that limestone was very much evident. It was thought that the oils that had penetrated the scaled surface had broken down in presence of the calcium hydroxide.

Wright Materials Laboratory used water alone for its GC/MS extraction. Comparing the mass spectra to library values revealed that the salts had been converted into hexanoic, octanoic, and decanoic acids, when mixed with concentrated hydrochloric acid. All of these acids are straight-chain fatty acids found in the esters of turboshaft oil (MIL-L-7808 or MIL-L-23699). Presence of these calcium salts in the damaged concrete proved that hydrolysis of the lubricants had occurred.

Carbonization in Field Concrete

XRD spectrometry of both sides of the scaled concrete specimens at Wright Laboratory revealed the presence of quartz and calcium carbonate, but not of calcium hydroxide. It appeared that the calcium hydroxide had been converted to limestone by the carbon dioxide made available as a by-product of burned hydrocarbons in the jet exhaust. As shown earlier in Figure 2, some of these scalings had aggregate embedded in them.

To confirm the carbonization of the old surface, a core from an undamaged area was cut into 6-mm (0.25-in.) slices that were treated with a solution of phenolphthalein and alcohol. If the solution contacts a base with a pH greater than 9, it will turn violet. The surface of the top slice did not change color, indicating that complete carbonation had occurred; however, its bottom and both sides of all the other slices turned almost completely violet, indicating the presence of the calcium hydroxide. SEM investigation of the bottom of the top slice revealed calcium hydroxide's classical hexagonal platelets (10), validating the phenolphthalein's indication of the presence of calcium hydroxide.

Treating the bottom of the scalings from the damaged area with phenolphthalein caused a few vague violet patches, but many clear areas; none of the exposed aggregate surfaces was violet. All of the hydroxyl ion had been consumed.

In short, IR and GC/MS showed that ester hydrolysis was occurring; XRD showed that calcium hydroxide had been depleted; and the SEM and phenolphthalein solution con-

firmed that calcium hydroxide had been consumed in the damaged concrete.

FAILURE MECHANISM

Role of Temperature and Carbonization

Heat from the APU plays a significant role in the damage process by accelerating the chemical reaction that ultimately leads to scaling of the concrete. A rule of thumb for any chemical reaction is that the reaction rate doubles for every increase in temperature of 10°C (18°F) (5).

An inspection of concrete eroded by spilled vegetable oils at neighborhood fast-food stores (Figure 4) indicated that hydrolysis of fatty oils by the hydroxyl ion does not have to have heat to occur. However, as seen in Figures 2 and 3, the



FIGURE 4 Hydrolysis of vegetable oils by newer pavement.

older pavements investigated during this study were scaling instead of eroding. This scaling always appeared to originate from weakened planes beneath the surface layer of concrete. As stated earlier, IR and phenolphthalein tests showed that the calcium hydroxide on the surface of these old pavements had already been depleted through contact with carbon dioxide to form a thin layer of calcium carbonate that did not react with spilled oils under the aircraft.

Thermal Cycling Enables the Process

To explain how the oils established contact with the calcium hydroxide just below the surface of the concrete, the following was observed from the field cores, but has not been verified. With the application of heat, the free moisture in the top 6 to 13 mm (0.25 to 0.50 in.) on the concrete is driven out. After the heat is removed and the pavement begins to cool, lubricating oils and hydraulic fluids on the surface as well as free moisture from within the concrete are sucked into the upper layers of the pavement. Rock or concrete with a liquid saturation of 0.2 percent or less has been reported to have suction pressures on the order of 10 MPa (1,450 psi) (11). When the APU is again fired up, the penetrating heat reaches the calcium hydroxide in solution, it hydrolyzes the esters in the absorbed fluids, liberating alcohol and forming calcium salts of the carboxylic (fatty) acids. For extensive heat durations (tens of minutes) and surface temperatures exceeding 100°C (212°F), the liquid moisture is converted to steam, expelling the oils, and the salts of the fatty acids are precipitated out in solid form. Upon cooling, the process repeats itself, and new oils are sucked in from top and water from below.

Role of Calcium Hydroxide

The hydroxyl ion is being consumed in each cycle. It is thought that calcium hydroxide provides one source of base for the

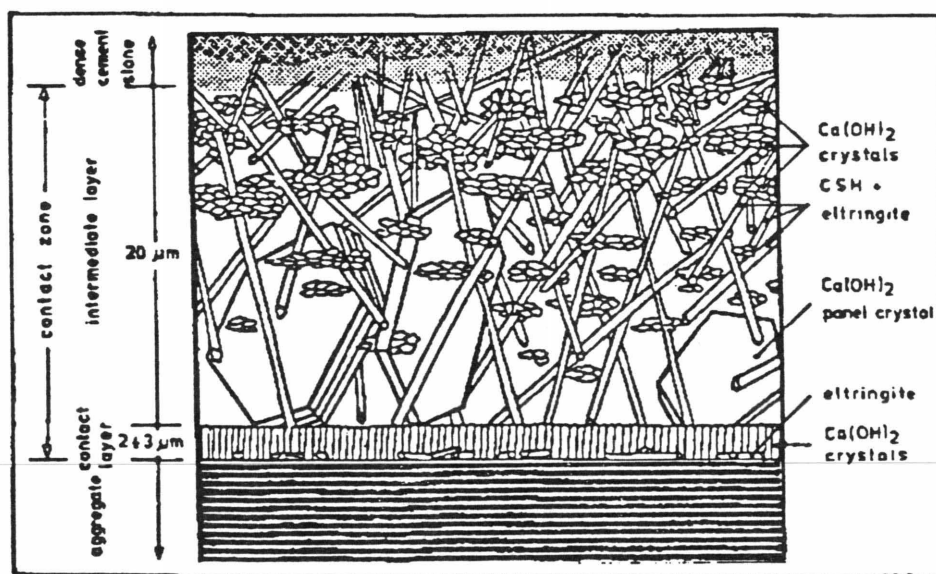


FIGURE 5 Model of paste-aggregate interface (9).

hydrolysis, to form the alcohol and the calcium salt of the fatty acid. The salts are soft, slightly soluble, and white (unless they have a red tinge from dye in hydraulic fluid). These salts replace the calcium hydroxide crystals. Damage may take months to become evident because of the low solubility of calcium hydroxide in water, limiting its availability for reaction.

Figure 5 illustrates the contact between the cement mortar (calcium silicate hydrate) and the aggregate in an early stage of the hydration process (9). With time and increased hydration the intermediate layer is overlapped by more of the panel-shaped calcium hydroxide crystals and the cement mortar. Zimbelmann states that the load transfer between the cement mortar and the aggregate is provided mainly by the large hexagonal platelets of calcium hydroxide (9). Both the contact layer around the aggregate and the large platelets of calcium hydroxide are probably being consumed in the hydrolysis process.

The hydroxyl ion can also come from the hydrated silicate and aluminate phases of the cement. Here, the calcium silicate hydrate cement decalcifies and converts to a highly porous form of silica.

Onset of Scaling

Eventually, as the available hydroxide is depleted, thermal differential stresses and aircraft loads will exceed the strength

of the weakened mortar-aggregate bonds and cause planar failure or scaling 6 to 13 cm (0.25 to 0.50 in.) thick.

FINDING REPLACEMENT MATERIALS

After establishing that hydrolysis was leading to scaling, the search for a solution focused on finding materials that would either delay or stop the reaction. Since scaling takes months to materialize in the field, a laboratory testing scheme was developed that could replicate and accelerate field conditions.

Laboratory Setup

The laboratory setup included the use of Erlenmeyer flasks (for crushed material) and kettles (for solid pieces) that could simulate (in reaction vessels) the mixing and refluxing of oils and water that takes place in the field at elevated temperatures (Figure 6). Up to 24 vessels could be used simultaneously; each vessel could independently test a different material at controlled temperatures. After the material hydrolyzed, the

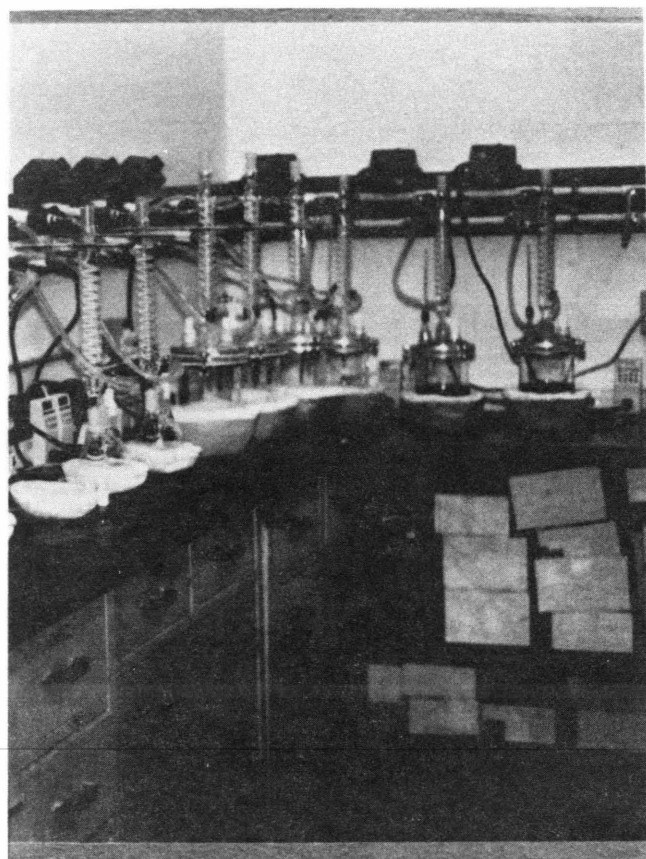


FIGURE 6 Laboratory setup to replicate field damage.

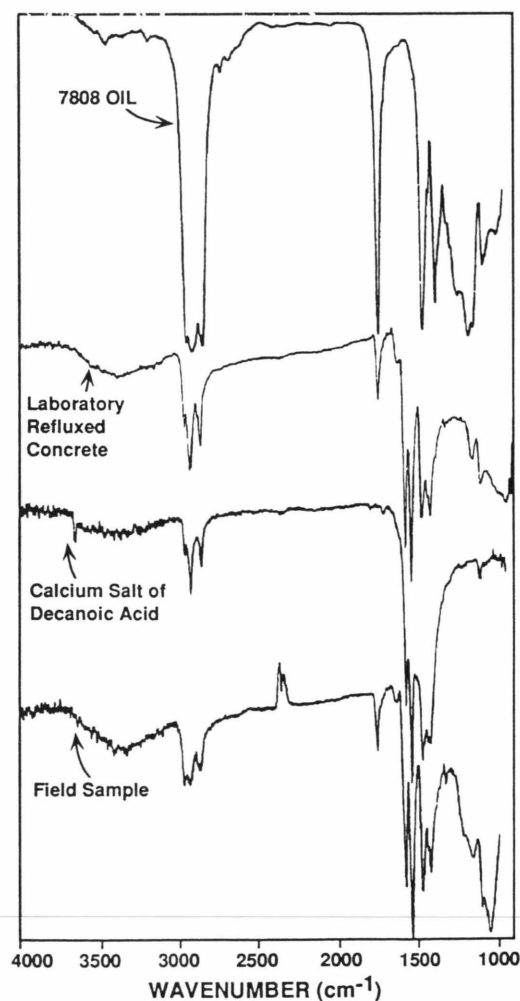


FIGURE 7 FTIR spectra for laboratory and field samples.

products formed were identified using Fourier transform infrared (FTIR) analysis. Next, cylinders 2.5 cm (1 in.) across and 5.1 cm (2 in.) high were tested. The cylinders were either sliced and run through the FTIR using a contact sampler or used for unconfined compressive strength tests.

Initial Tests

Tests initially compared field scalings with laboratory concrete made from finely crushed quartz aggregate and a water-cement ratio of 0.5. The vessel contained 10 percent concrete, 20 percent oil, and 70 percent water by volume. After five 24-hr days of refluxing, FTIR analysis of the hydrolyzed products formed are shown in Figure 7. The characteristic peak of calcium hydroxide shown in the laboratory sample was absent in the field scalings, indicating that it had been consumed by carbonation or ester hydrolysis. In addition, the acid spectra from both the laboratory and field samples matched. The lab sample shows approximately twice as much transmittance as the field sample, indicating twice the number of salts. This verified that the experimental technique was performing as designed. Therefore, any material could be quickly and accurately assessed for ester hydrolysis.

Screening Replacement Materials

A number of materials ranging from lower to neutral pH binders were evaluated in the laboratory. Table 1 identifies the pH of the refluxed liquids after 3 days and indicates if any fatty acid salts were generated. Four replacement materials did not hydrolyze: three acid-base cements and a Furan polymer. Generally, an 18 percent loss in strength occurred for all specimens that salted. On the basis of this laboratory

screening, all three acid-base cements have been placed at both B-1 and F/A-18 locations and are undergoing evaluation.

CONCLUSIONS

Concrete damage to B-1 and F/A-18 parking aprons in the vicinity of APU impingement is caused by the chemical reaction (hydrolysis) between spilled lubricating and hydraulic oils and the hydroxyl ion in the cement. Cyclic heating from the APU makes it possible for the oils to penetrate the concrete accelerating the hydrolysis process, which transforms the calcium around the aggregate and in the paste into salts of fatty acids, destroying the paste-aggregate bond. Evidence shows that the degree to which the concrete is damaged depends on the ability of the oils to penetrate. Therefore, it is believed that more permeable concretes incur more damage. Because of the carbonation of the surface of older pavements, oils must penetrate deeper to cause damage.

It is inferred that any hydraulic concrete system, whether acid or base, will hydrolyze and scale if jet oils are allowed to penetrate. The simplest solution to this problem is to keep all the lubricating and hydraulic oils off the pavement, especially in the vicinity of heat impingement. APU temperatures are not high enough, by themselves, to damage concrete. If oils cannot be kept off the pavement, the heat should not be allowed to impinge onto the spill areas since heat facilitates and accelerates the hydrolysis process. The use of steel plates appears to be working at Dyess Air Force Base and Cecil Field because the pavement is shielded from this heat.

Finally, the cement binder might be replaced by a neutral (or close to neutral) material with a pH between 6 and 8, such as a polymer concrete, phosphatic concrete, or ceramic. Several candidate materials in this category have already passed

TABLE 1 Change in pH of Replacement Materials

Sample	Before	After	Salt Generated
OPC	12.3	8.0	Yes
Magnesium Phosphate	8.7	8.1	No
Alumina Phosphate	5.6	5.2	No
Phoscrete (Magnesium & Alum.)	8.0	8.3	No
Furfuryl Alcohol	4.3	4.3	No
High Carbon OPC	12.2	11.2	Yes
10% Polyvinyl Alcohol Modified OPC	12.0	9.4	Yes
Calcium Sulfate	12.0	7.8	Yes
Room Curable Ceramic	11.0	8.5	Yes

NOTE: OPC = ordinary portland cement.

laboratory screening tests, have been placed in the field, and are undergoing evaluation.

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