Though portland cement concrete is a highly-durable structural material, certain physical and chemical actions can render it unserviceable long before it has reached its design life. Accelerated deterioration can occur on exposure to harsh chemicals such as acids and sulfates. Because the costs associated with premature failure are high, there is considerable incentive for developing ways to predict and prevent deterioration.

Rapid deterioration is often attributed to inadequate mix proportions, improper cement types, low-quality aggregates or poor workmanship. Avoiding these factors may well eliminate or mitigate deterioration. However, some environments are so aggressive that additional steps are needed to insure durability. Specialty cements, various admixtures, pozzolans, coatings and surface treatments are some of the options that have been used with varying degrees of success. This bulletin describes the use of microsilica (also known as silica fume) for reducing the dete-
ioration of concrete by chemical attack. Deterioration is defined as the degradation of the concrete material itself.

Mechanisms of Deterioration
Deterioration of concrete can be discussed in terms of two mechanisms: the removal of material from the cement paste by dissolution, and the expansion of material within the concrete.

Dissolution
In this process, a solvent dissolves soluble material and removes it from the concrete matrix. As a result, the concrete becomes more porous, the rate of dissolution increases, and the concrete may ultimately disintegrate. The material removed may be a substance normally present in concrete such as calcium hydroxide, or may be formed by a chemical reaction that occurs on exposure of the concrete to external media. Dissolution without chemical reaction is often referred to as leaching. Removal of the calcium hydroxide in the cement paste by permeating water is an example of leaching. The deterioration of concrete exposed to hydrochloric acid is an example of dissolution by chemical reaction. The acid reacts with the calcium hydroxide to form calcium chloride which dissolves in the acid solution and is carried away. If the reaction products are readily-soluble, as in the case of calcium chloride, deterioration can be rapid and more severe than occurs with the leaching of calcium hydroxide which is only moderately soluble.

Another example of chemical attack is found in sewage lines where hydrogen sulfide (H\textsubscript{2}S) is formed by the action of anaerobic, sulfur-reducing bacteria. This gas is then oxidized to sulfuric acid by aerobic bacteria and in turn reacts with the alkaline paste of concrete.

Expansion
Cracking and spalling result if a chemical reaction causes a pressure increase within the concrete matrix. This can occur if the reaction products are insoluble and occupy a greater volume than the original substance. Expansive reaction examples are attack by sulfates, alkali-silica reactions and freeze-thaw deterioration.

Rate of Deterioration
Knowing the rate of deterioration is essential to predicting the life expectancy of concrete structures exposed to various attacking media. Because the rate of attack is affected by a host of factors, it is usually only possible to predict deterioration in qualitative terms. Some of the most important factors are discussed below.

Permeability of Concrete
Concrete permeability plays a major role in determining the rate of deterioration caused by external agents. It affects the depth to which the attack occurs, the amount of susceptible material exposed to the attacking medium, how rapidly the attacking medium is replenished in the attack zone and how quickly materials are leached from the interior of the concrete. The higher the permeability, the greater the rate of attack. This also applies to concretes only partially exposed to the attacking medium. Permeability is not necessarily related to porosity but is dependent on the geometry of the pores and the pore size distribution.

If the concrete is impermeable, the attack will be relatively superficial and limited to the surface. Attack within the concrete will be governed by molecular diffusion which is much slower than convective processes. The use of low-permeability concrete is the primary means of preventing or minimizing the effects of external attack.

Quantity of Aggressive Material
Just as the amount of material that is exposed to attack affects the rate of attack, so does the amount of attacking agent. The more concentrated the chemical is in the attacking medium, the greater its capacity for doing damage.

The mode of exposure is also important. Cyclic exposure with alternate wetting and drying of the concrete may be even more detrimental than continuous exposure to the attacking medium.

Solubility
The solubility of the reactant products also affects the rate of attack, and in some cases may actually be the major factor controlling the degree of deterioration. Clearly, the more soluble the concrete
component is in the attacking medium, the greater the amount of material that will be removed and the faster the rate of deterioration.

**Temperature**
The rate of chemical reaction increases exponentially with temperature (approximately doubling for each 10°C [50°F] increase), so the rate of chemical attack on concrete can also be expected to increase with temperature.

**Abrasion**
Abrasion increases the amount of concrete exposed to the aggressive medium and also promotes the removal of material weakened by chemical attack. As a result, the rate of deterioration is accelerated. Factory floors and pipelines are examples of how deterioration can result from the combined action of abrasion and chemical attack.

**Reducing Degradation**
The first line of defense against aggressive chemicals of all types is to decrease the permeability of the concrete. This reduces the amount of concrete exposed to attack at any one time by slowing the permeation of the aggressive agents into the bulk of the concrete. Reducing the water/cement ratio of concrete is one means of reducing permeability. However, if an aggressive agent is attacking and deteriorating the cement paste in concrete, then using a higher cement factor to lower the water/cement ratio can be counterproductive, since this will result in more material to be attacked. Therefore, the use of superplasticizers is essential to attain low water/cement ratios while minimizing the necessary increase in cement factors. The addition of microsilica to low water/

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**Table 1**

<table>
<thead>
<tr>
<th>Acid (Category)</th>
<th>Chemical Formula</th>
<th>pH @ Various Concentrations</th>
<th>Typical Applications</th>
<th>Effect of Microsilica</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetic acid (organic)</td>
<td>C₂H₃O₂H</td>
<td>2.7 2.4 2.2</td>
<td>fermented products — wineries, breweries, cider, vinegars, acetate plastics — vinyl, rayon, and cellulose food preservatives — meat packing, photographic chemicals, rubber latex, insecticides</td>
<td>Dramatic improvements are possible, see Figures 1 &amp; 3</td>
</tr>
<tr>
<td>Formic acid (organic)</td>
<td>CHO₂H</td>
<td>2.2 1.85 1.7</td>
<td>dye industry, tanning, electroplating, insecticides, rubber latex, animal feed, chemical plants</td>
<td>Dramatic improvements are possible, see Figures 2 &amp; 4</td>
</tr>
<tr>
<td>Hydrochloric acid</td>
<td>HCl</td>
<td>0.5</td>
<td>ore refining, pickling and cleaning of metals, food processing, chemical plants</td>
<td>Very little improvement at pH &lt;1.0</td>
</tr>
<tr>
<td>Lactic acid (organic)</td>
<td>C₃H₅O₃H</td>
<td>2.4 2.1 1.9</td>
<td>food products, dairy products, breweries, pulp and paper</td>
<td>Tested by Mehta (Reference 1) showed 15% microsilica to have double the life span of reference in 1% lactic acid</td>
</tr>
<tr>
<td>Phosphoric acid</td>
<td>H₃PO₄</td>
<td>1.6 1.2 1.0</td>
<td>phosphate-based fertilizers, detergents, soft drinks, rustproofing metals, chemical plants</td>
<td>Slight to moderate improvement for 5% concentrations. See Figure 5</td>
</tr>
<tr>
<td>Sulfuric acid</td>
<td>H₂SO₄</td>
<td>1.0 0.5 0.3</td>
<td>fertilizers, explosives, oil refining, metals processing, coal/coke handling facilities, textiles, pulp and paper, sewage pipe</td>
<td>Moderate improvement at 1% concentration, little improvement at higher concentrations. See Figures 6 &amp; 7</td>
</tr>
</tbody>
</table>
Cement ratio concrete has been shown to dramatically reduce permeability below the level made possible by lowering the water/cement ratio. When deterioration is due to expansive forces, the use of air entrainment and/or porous aggregates can reduce deterioration by providing areas for expansive product accumulation without the resultant build-up of internal stresses.

Another important factor in reducing deterioration is the correct selection of aggregate type. In general, siliceous aggregates are less susceptible to acid attack, and calcareous aggregates are less susceptible to alkaline attack. However, calcareous aggregates are used in situations such as sewer pipes where they help to neutralize small quantities of relatively aggressive acid. In sewer pipe, under certain conditions, the crown of the pipe is continually exposed to relatively small quantities of sulfuric acid. In this environment, the calcareous aggregate is used so that the small quantities of acid will evenly attack all of the concrete surface and be neutralized before significantly penetrating into the concrete depth. If non-reactive, siliceous aggregates are used in this situation, the acid just attacks the cement paste. Without the calcareous aggregate, not as much reactive material is available on the surface. The acid then penetrates deeper into the concrete, resulting in increased depth of degradation.

* All microsilica dosages are listed as percent by weight of cement.
Microsilica

Microsilica enhances the durability of concrete in several ways:

- By reducing the permeability of the concrete.
- By reducing the calcium hydroxide content of the concrete.
- By producing a more stable, highly polymerized C-S-H (calcium silicate hydrate) paste which more effectively ties up alkali and aluminum ions, making them less available for reaction.

These enhancements to concrete durability are due to microsilica’s extremely fine particle size and its properties as a highly-reactive pozzolan. (See Engineering Bulletin Number One, “Force 10,000 Microsilica and Its Uses in Concrete”). The effect of lower permeability has already been discussed. The effect of reducing the calcium hydroxide is very important, since it is the concrete component that is most readily attacked, especially in acidic solutions.

When ordinary portland cement hydrates, up to 25 percent of the resultant cement paste may be composed of calcium hydroxide. This product does not contribute to strength and is readily attacked by acidic solutions and by sulfates. Therefore, even in concrete with low permeability, the ability of acids to attack and remove the calcium hydroxide allows a means of ingress of the attacking agent into the bulk of the concrete, resulting in higher porosity of the concrete. As it turns out, many of the structured calcium hydroxide deposits in concrete form at the paste-to-aggregate interface. As this material is attacked, the voids around the aggregate increase, resulting in reduced aggregate bond, lower strengths and a greater possibility of aggregate pop-out, especially under abrasive forces.

Microsilica reduces the calcium hydroxide content by reacting with it to produce more C-S-H paste. The net result is a concrete with greatly reduced permeability in the bulk paste and a greatly reduced amount of “ingress shortcuts” provided by the calcium hydroxide. In addition, the C-S-H paste formed from microsilica is more stable in low pH environments and can more effectively tie up alkali and aluminum ions. The resulting concrete is more resistant to moderately aggressive acid attack (pH > 1.0), alkali-aggregate attack and most types of sulfate attack.
Aggressive Chemical Test Program
Microsilica concrete at various dosage rates and a reference concrete were exposed to the following acids:

<table>
<thead>
<tr>
<th>ACID</th>
<th>pH</th>
<th>Fig.</th>
</tr>
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<tbody>
<tr>
<td>5% Acetic</td>
<td>2.4</td>
<td>1 &amp; 3</td>
</tr>
<tr>
<td>5% Formic</td>
<td>1.85</td>
<td>2 &amp; 4</td>
</tr>
<tr>
<td>5% Phosphoric</td>
<td>1.2</td>
<td>5</td>
</tr>
<tr>
<td>1% Sulfuric</td>
<td>1.0</td>
<td>6</td>
</tr>
<tr>
<td>5% Sulfuric</td>
<td>0.5</td>
<td>7</td>
</tr>
</tbody>
</table>

These acids were chosen to cover a range of aggressive pH environments, and because they are acids that are commonly used in industry (see Table 1).

A water/cement ratio of 0.36 was used for most tests except for a 0.26 mix for the 5% formic acid test. Microsilica dosage rates ranged from 0-30%. Aggregate used was trap rock or river gravel.

Concrete cylinders (75 mm x 150 mm [3 in. x 6 in.]) were made from each mix and moist cured for 28 days. The cylinders were initially weighed, submerged in acid for two weeks, removed, wire-brushed, allowed to dry for two weeks and weighed again (one complete cycle). The results of these weight-loss tests are in Figures 3 through 7.

Conclusions
Many variables affect the rate at which different chemicals attack and deteriorate concrete. For greater durability in any environment, the first line of defense is good quality, low water/cement ratio concrete. The addition of Force 10,000 microsilica can increase the resistance of quality concrete to several aggressive chemical environments.

Reduced concrete permeability and the reduction of free calcium hydroxide are the key reasons why microsilica concrete has increased resistance to moderately aggressive acid attack. Figures 3 & 4 show dramatically improved resistance to organic acid environments with pH > 1.8 for microsilica concrete versus the reference. Figures 5 through 7 show improvements with microsilica concrete, but they are less dramatic as the pH is reduced. Higher dosage rates of microsilica produce more acid-resistant concrete.

Microsilica does not produce concrete which is completely impervious to chemical attack but does significantly expand the realm of environments where concrete can perform satisfactorily without surface protection. Since most aggressive mediums are a combination of many chemicals, it is imperative that microsilica concrete be tested by exposure to those chemicals at the site before a decision is made to use this type of concrete.

Grace cannot guarantee the durability of Force 10,000 concrete to chemical attack. The design engineer must first test it in these environments to be assured that it will perform adequately. As with all concretes, Force 10,000 concrete must be mixed, placed and finished according to proper ACI guidelines. However, for chemical resistance, this concrete must be moist-cured for 28 days.

References