Effect of Nitric Acid Concentration on the Compressive Strength of Laterized Concrete

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Abstract
Laterized concrete is concrete in which some or all of the fine aggregates is from laterite. In this study, the effects of varying nitric acid concentrations (0%, 5%, 10%, 15%, and 20%), mix proportions (1:1:2, 1:1½:3), exposure period (28, 56, and 84 days) and percentage laterite content (0%, 25%, and 50%) on the compressive strength of laterized concrete were investigated. The tests were carried out with a view to simulating the performance of laterized concrete in contact with soluble nitrate-based substances. 100x100x100mm cubes of laterized concrete were cast and moist-cured for 28 days and the strength of concrete at this age was determined. The cubes were thereafter immersed in 0%, 5%, 10%, 15%, and 20% concentrations of nitric acid for a total of 84 days. Compressive strength tests were carried out at the end of 28 days, 56 days and 84 days of immersion. The results of the tests indicated that the compressive strength significantly reduces with increase in acid concentration, immersion period and laterite content. The effect of richness of mix on resistance of laterized concrete to the acidic aggression becomes more pronounced at the highest (50%) laterite content.

Keyword: compressive strength, laterized concrete, nitric acid concentrations, percentage laterite content.

1. Introduction
Laterized concrete is concrete in which laterite fines are used partially or wholly to replace the conventional sand. Laterite occurs in large quantities and in different types in the tropics, including Nigeria. Research has shown that laterite could be used to effectively replace sand up to 50% in structural concrete. Compressive strengths in the range of 10MPa to 40MPa has been reported in literatures for laterized concrete prepared from nominal structural concrete mixes (Olusola et al., 2002; Osunade, 2002; Salau, 2003; Olusola, 2005; Udoeyo et al., 2010a and 2010b; Olawuyi et al., 2012). A major consideration in the use of any type of concrete is its quality which is largely determined by its constituent materials. Such measures of qualities include satisfactory performance in compressive strength and environmental durability requirements. Effects of corrosive substances such as alkalis, sulphuric acid (H2SO4) and corrosive salts such as sulphates and chlorides when present in solutions on concrete have attracted a lot of attention from researchers. However, effects of nitrates and nitric acid (HNO3) solutions appear to have been given less attention (Mtallib, 2002). Bickzack (1967) reported that most of the salts of HNO3 with the exception of ammonium nitrate (NH4NO3) are not detrimental to concrete at very low concentrations; NH4NO3 has been observed to be very aggressive to all concrete and mortars.

Nitric acid can be formed from the compounds and radicals of nitrates in the presence of water and this is largely responsible for the corrosion of concrete (Musa, 1992). Nitric acid occurs in chemical plants producing explosives, artificial manure and similar products. Though HNO3 is not as strong as H2SO4, its effect on concrete at brief exposure is more destructive since it transforms the calcium hydroxide [Ca(OH)2] of concrete into the highly soluble calcium nitrate salt and a low soluble calcium nitroaluminate hydrate. The process can be represented by the equations below.

\[ 2\text{HNO}_3 + \text{Ca(OH)}_2 \rightarrow \text{Ca(NO}_3)_2\cdot2\text{H}_2\text{O} \text{ [Calcium nitrate]} \]

\[ \text{Ca(NO}_3)_2\cdot2\text{H}_2\text{O} + 3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot8\text{H}_2\text{O} \rightarrow 3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Ca(NO}_3)_2\cdot10\text{H}_2\text{O} \text{ [Calcium nitroaluminate hydrate]} \]

Mtallib (2002) investigated the compressive strength of regular concrete in contact with nitrate-based substances and concluded that there was a reduction in the compressive strength for all specimens in contact with varying concentrations of HNO3.
Using procedures similar to that adopted by Mtallib (2002), the present study aims at investigating the compressive strength of laterized concrete exposed to varying concentrations of nitric acid with a view to determining its durability performance when in contact with nitrate-based substances.

2. Experimental Procedure

2.1 Materials

The basic materials used in this study are laterite, riversand, both of which were used as fine aggregates, washed gravel used as coarse aggregate, ordinary Portland cement (OPC) of strength class 32.5 (conforming to the requirements of Nigerian Industrial Standard, NIS444-1:2003, and British standard, BS EN 197-1:2000) used as binder and tap water. The choice of this strength class as opposed to strength class 42.5 for concrete structural purposes was made to simulate the common uninformed practice on most low-rise building construction sites. The use of both strength classes has been adopted in a more elaborate on-going further study on acid resistance of laterized concrete. The summary of the physical properties of the soil samples used are shown in Table 1. The listed values indicate that all the soil gradations conform to BS 882: 1992 gradation limits for aggregates and are suitable for concreting. Two common nominal mix ratios namely 1:1:2 and 1:1.5:3 having laterite as substitutes for sand in the fine aggregates fraction in gradation of 0%, 25%, and 50% were used in each case. The water/cement ratios of the selected mixes determined from the results of a previous research (Olusola, 2005).

For the respective laterite fractions are 0.45, 0.55, and 0.60 for mix proportion 1:1:2 and 0.65, 0.65 and 0.70 for mix proportion 1:1.5:3. The laterized concrete mixes and 100mm cubes were prepared and cast respectively in accordance with the provisions of BS EN 12390-3:2002). Three replicates were used in each case. The method of curing involves covering the cubes with sacks which were kept consistently moistened for 21 days. This method of curing, instead of complete immersion in water simulates one of the best site-curing conditions (Mtallib, 2002). The concrete cubes were then air-dried in the laboratory for 7 days to ensure that there was no pore-water in the concrete during testing.

Slump test (in accordance with BS EN 12350-2:2009) was carried out to measure the workability of all concrete mixes. At the end of 28 days of casting and moist curing, three cubes were randomly selected from each of the concrete mixes and tested for the compressive strength. The acid- water proportions required for 0%, 5%, 10%, 15%, and 20% acid concentrations were volumetrically determined. The concrete cubes were immersed in the various nitric acid concentrations. At the end of the immersion periods of 28 days, 56 days, and 84 days, three cubes were removed from each of the different concentrations of the acid medium, thoroughly rinsed with tap water and air dried in the laboratory for some hours before testing for their compressive strengths. In addition, further assessments of the performance of the specimen were made from visual assessment, mass loss and strength deterioration factor (SDF). This follows the approach used by Sivakumar and Murthi (2008) and Hewayde et al., (2007).

The visual observation of acid attack was made using a performance scale of 0 for no attack, 1 for very slight attack, 2 for slight attack, 3 for moderate attack, 4 for severe attack, 5 for very severe attack and 6 for partial disintegration (Al- Tamini and Sonebi, 2003).

The percentage of mass loss at the end of each immersion period was calculated according to Equation 1.

\[
\text{Mass loss \%} = \left((M_1 - M_2)/M_1\right) \times 100
\]  

\[\text{Where,}\]

\[M_1 = \text{Mass of specimen before immersion}\]

\[M_2 = \text{Mass of specimen at the end of immersion period}\]

The Strength Deterioration Factor (SDF) which is a measure of the reduction in compressive strength was calculated using Equation 2. (Bai et al., 2003; Han-Young Moon et al., 2003, Hewayde et al., 2007 and Sivakumer and Murthi, 2008).

\[
\text{SDF} = \left[(f_{c128} - f_{ca})/ f_{c128}\right] \times 100
\]  

\[\text{Where,}\]

\[f_{c128} = \text{Compressive strength at 28 days}\]

\[f_{ca} = \text{Compressive strength at acid attack}\]
\( f_{c128} \) = average compressive strength of moistened concrete cubes at first 28 days.

\( f_{ca} \) = average compressive strength of concrete cubes immersed in the acid solutions.

It should be noted that the concentrations of acid used in this study are on the high side. This parameter has to be adjusted in order to accelerate the degradation and obtain results more rapidly within the 84 days of exposure. Despite its shortcomings, this approach has the advantage that the entire life of the specimens in question can be simulated. Further studies that make use of more realistic lower acid concentrations for much longer immersion periods (over one year) is on-going.

3. Results and Discussion

3.1 Visual Assessment

Table 2 shows the summary of the visual assessment of the cube specimens after 84 days (12 weeks) of immersion in the various nitric acid concentrations. The specimens immersed in water did not show any visible sign of deterioration after the 84-day immersion period. From Table 2, it was observed that the laterized concrete concrete specimens prepared from mix 1:1:5:3 suffered a greater degree of acid attack than those prepared from 1:1:2 concrete mix in all the acid solutions. The mixes having 50% laterite content were the most affected. The deterioration of the laterized concrete mix specimen ranges from moderate to very severe attack. The edges and surfaces of specimens attacked severely and very severely disintegrated visibly with brownish grease like substance (dotted at intervals with greenish patches) deposited on the surface of the immersed specimen. It is thus possible that nitric acid attack on laterized concrete could be recognized by brownish coloured gel with few greenish patches on the surface of the concrete.

2.2 Strength Deterioration Factor (SDF)

The compressive strength increased throughout the immersion period for the zero percentage concentration of the acid. As shown in Table 3, the specimens continuously cured in water after the first 28 days of moist curing exhibited slightly higher compressive strength than those continuously cured in moist conditions. This observation agrees with earlier assertions by Olusola (2005) that curing by complete immersion in water is the best for beneficial strength gain for laterized concrete specimens.

The SDF (Table 3) increase with increasing concentration of acid. The deterioration of both the concrete (0% laterite content) and laterized concrete specimens (25% and 50% laterite contents) within the first 28 days of immersion in all acid concentrations investigated is far greater than during the subsequent immersion periods. More than 50% of the total SDF observed at the end of the 84 days occurred within the first 28 days in the 5% acid concentrations. This could be attributed to the fact that the strength of the acid at 5% concentration would have been highly reduced during the first 28 days of immersion resulting in a milder attack on the laterized concrete during the remaining period of immersion. Similar observations had earlier been made by Mtallib (2002) with normal concrete specimens. The pattern of variation of SDF with immersion period at 5% acid concentration is similar to what was observed in all other acid concentrations (10%-20%), although higher values of SDF were recorded for the latter. For these concentrations, not less than 70% of the 84-day deterioration occurred within the first 28 days of immersion. In other words, as immersion period increases, SDF increases but not proportionately.

The observation might be attributed to the fact that at 56 days, the surfaces of the laterized concrete cube specimens were temporarily protected by the brownish, gel-like deposit surrounding, the cubes, hence reducing the acid aggression beyond the 56 days of immersion.

Figures 1-6 shows that the compressive strength of the tested concrete and laterized concrete cubes decreases as acid concentration increases. In addition, Table 3 further reveals that the higher the concentration of the acid, the greater the SDF of the tested specimens. The SDF, however, does not appear to be directly proportional to the concentration of the acid. For example, at 20% acid concentration and for 1:1:2 mix, 25% laterite content, the calculated SDF was obtained as 54.3% at the end of 28 days of immersion in acid; whereas at 5% concentration, (1/4 of 20%) for the same parameters, the SDF was obtained as 26.6% (approximately half of SDF at 20% concentration).

Also, from Figures 1-6, the compressive strength of cubes immersed in the various acid solutions for all mixes decreases with increasing immersion period. It is noted that the acid is not being renewed at the end of every 28 days
and no mechanical agitation was involved. Since only chemical action is present, a slowly growing layer of degraded material is formed and this might have slowed down further reactions. If chemical action had been combined with mechanical action, abrasion might have helped to remove the degraded layer and leave a new surface to increasing chemical attack as immersion period increases while the pH of the acid solutions are averagely maintained.

It is further observed from Table 3 and Figures 1-6 that the richness of the mix does not have an appreciable influence on the SDF, and hence on the resistance of the concrete and laterized concrete specimens to the aggressive action of the nitric acid solution of varying concentrations. Mixes of comparable compressive strength, for example at 25% laterite content for mix 1:1.5:3 and 50% laterite content for mix 1:1:2, the rate of deterioration at all acid concentrations observed from Table 3 appears to be similar and may thus be independent of the aggregate/cement ratio; it is however noted that the mix 1:1:2 at 50% laterite content with higher compressive strength values exhibited slightly higher values of SDF at all levels of acid concentration investigated. This observation will probably be the result of the combined influence of richness and percentage laterite content of the mixes.

Table 3 further shows that, except in some few cases, the higher the percentage laterite content for each mix ratio, the lower the SDF at all acid concentration levels. However, this does not translate to higher compressive strength at increasing laterite content in an acidic environment. Rather, the test results only showed that there was a decrease in rate of strength reduction as laterite content increases. Ordinarily, richer mixes, that is, higher compressive strength mixes are expected to offer greater resistance to acid attack; hence such should exhibit lower SDF. It appears that the introduction of laterite into the concrete mixture altered the expected pattern of variation. When normally cured in water, concrete exhibits higher compressive strength at a specified age than laterized concrete prepared from the same mix. This have been attributed by Olusola (2005) to higher rate of cement hydration in the conventional concrete and presence of river sand which is composed of almost 99% silica (which is almost a pure quartz material—a stiff, stable, lowly porous, high compressive strength material). On the other hand, in laterized concrete, a percentage of the river sand content has been replaced by laterite which contain about 63% silica and has a higher loss on ignition (LOI) close to 9% compared to the cleaner sand whose LOI is often less than 1% (Olusola, 2005). Thus, in laterized concrete, lesser quantities of silicate and calcium ions are produced at a slower rate.

This, in effect might reduce the rate of attack by acid. At any particular age, there will be more of calcium hydroxide available for reaction with the acid resulting in the higher rate of deterioration in the normal concrete than in laterized concrete. Usually, an acid attack is diagnosed primarily by two main features; absence of calcium hydroxide in the cement paste and surface distribution of cement paste exposing aggregate. This observation about laterized concrete needs further investigation.

### 2.3 Mass Loss.

Generally, percentage mass loss after a period of immersion increases with acid concentration and immersion period for each mix and at each laterite content investigated. For mix 1:1:2 and between 0% and 25% laterite content, the mass loss increases as laterite content increases. However, beyond 25% laterite content, the mass loss decreases. This was clearly observed from Table 3 at 5% and 10% acid concentrations. Similarly, this second pattern was also exhibited by the lesser rich mix 1:1:5:3. Again, the influence of incorporating laterite in concrete on the acid resistance of the resulting laterized concrete is evident. Table 3 shows that more than 10% loss in mass due to immersion in all the nitric acid solutions was recorded after 28 days immersion period for the two mixes tested.

### 3. Conclusions

The following conclusions are drawn from the result of the investigations:

- The specimens immersed in water did not show any visible sign of deterioration after the 84-day immersion period but rather show continuous improvement in compressive strength.
- Visual assessments showed that the laterized concrete specimens having higher laterite content for each of the two mix ratios investigated experience greater deterioration when immersed in nitric acid solutions.
- The compressive strength of both the concrete and laterized concrete specimens decreased with increasing acid concentration, immersion period and laterite content.
Laterized concrete cubes continuously cured in water exhibited higher compressive strength than those continuously moist-cured.

The higher the concentration of the acid, the greater the SDF; however, the SDF is not directly proportional to the concentration of the acid.

The SDF of the tested specimens increased with increasing immersion period in nitric acid solutions; however, the SDF is not directly proportional to the immersion period.

More than 50% and 70% of the total SDF calculated at the end of the 84-day immersion period occurred within the first 28 days of immersion in 5% and higher acid concentrations respectively.

Hence, five percent concentration of the acid (which is realistic practically) within 28 days of immersion significantly reduced the compressive strength of both concrete and laterized concrete to a very low value in each case.

The rate of deterioration of mixes of comparable strength appears to be similar and may be independent of the aggregate/cement ratio alone.

The combined effect of richness of mix and laterite content on resistance of laterized concrete to nitric acid attack becomes more pronounced at the highest 50% laterite content. Generally, the higher the percentage laterite content for each mix ratio, the lower the SDF at all acid concentration levels. It appears increasing laterite content slows down the rate of acid attack.

The use of 20% nitric acid concentration for accelerated test in this study appears unrealistic and is on the very high side.

Generally, the percentage mass loss after a period of immersion increases with nitric acid concentration and immersion period for each mix and at each laterite content investigated.

More than 10% loss in mass due to immersion in nitric acid solutions was recorded after 28 days for the two mixes investigated.

4. Recommendations.

1. The study has shown that laterized concrete is highly vulnerable to acid attack. Hence, its use would be limited in environments exposed to nitrate-based substances. Probably, the use of water proofer and super plasticizer to enhance higher resistance to water absorption and higher compressive strength at lower water/cement ratio may serve to improve its performance in aggressive environment.

2. The long term (more than a year) acid resistance of laterized concrete at more realistic nitric acid concentrations less than or equal to 5% and at laterite contents between 0% and 50% measured in steps of 10% or less needs further investigation.

References.


Fig 1: Variation of compressive strength with acid concentration (mix ratio 1:1.5:3, 0% laterite content at 0.65w/c)
Fig 2: Variation of compressive strength with acid concentration (mix ratio 1:1.5:3, 25% laterite content at 0.65w/c)

Fig 3: Variation of compressive strength with acid concentration (mix ratio 1:1.5:3, 50% laterite content at 0.70w/c)

Fig 4: Variation of compressive strength with acid concentration (mix ratio 1:1:2, 0% laterite content at 0.45w/c)
Table 1: Summary of the physical properties of soil samples used.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Type of soil</th>
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<tbody>
<tr>
<td></td>
<td>Laterite</td>
</tr>
<tr>
<td>Fineness modulus, PM</td>
<td>3.03</td>
</tr>
<tr>
<td>Coefficient of uniformity, CU</td>
<td>4.96</td>
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<tr>
<td>Relative density</td>
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<tr>
<td>Water absorption (%)</td>
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<tr>
<td>Liquid limit LL (%)</td>
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<tr>
<td>Plastic limit PL (%)</td>
<td>17.5</td>
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<tr>
<td>Plasticity Index</td>
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</table>
Table 2: Visual assessment of laterized concrete deterioration level at end of 84 days immersion period of 28 days cured specimens.

<table>
<thead>
<tr>
<th>Mix proportion</th>
<th>% Laterite Content</th>
<th>Acid Concentration</th>
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<tbody>
<tr>
<td></td>
<td>0</td>
<td>5%</td>
</tr>
<tr>
<td>1:1:2</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>0</td>
</tr>
<tr>
<td>1:1.5:3</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>0</td>
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Table 3: Compressive strength, mass loss, and strength deterioration factor of laterised concrete exposed to varying nitric acid concentrations.

<table>
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<tr>
<th>MP</th>
<th>LC(%)</th>
<th>W/C</th>
<th>Slump (mm)</th>
<th>fc, 28 (N/mm²)</th>
<th>IP (days)</th>
<th>Compressive strength N/mm²</th>
<th>Acid concentration</th>
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</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Moist cured</td>
<td>water cured</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>SDF</td>
<td>ML</td>
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<tr>
<td>1:1:2</td>
<td>0</td>
<td>0.45</td>
<td>36</td>
<td>45.3</td>
<td>28</td>
<td>48.7</td>
<td>47.8</td>
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<tr>
<td></td>
<td>25</td>
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<td>33.5</td>
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<td>0.65</td>
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<td>28</td>
<td>32.0</td>
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<td>50</td>
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<td>28</td>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>56</td>
<td>27.0</td>
<td>28.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>84</td>
<td>30.8</td>
<td>31.7</td>
</tr>
</tbody>
</table>

MP: Mix proportions;  
LC: Laterite Content;  
W/C: Water/ Cement ratio;  
SDF: Strength Deterioration Factor;  
ML: Mass Loss and  
IP: Immersion Periods.
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