The purpose of this work is to study simultaneous influences of both microsilica and limestone powder, i.e. pozzolanicity and plasticity respectively, on important physicomechanical properties of fresh and hardened Portland cement paste. Different ternary mixes were prepared and studied by determining their relative workability, 7- and 50-day compressive strengths, water absorption, bulk specific gravity, and volume of permeable pore space. The obtained results confirm that the plasticizing effect of limestone powder makes it possible to replace Portland cement by a proportioned mixture of microsilica and limestone powder for improving the strength behavior at a constant W/C-ratio without any dispersing agent. It is also possible to produce ternary composite cements containing relatively high contents of microsilica and limestone powder with no considerable loss in both workability and compressive strength compared to plain Portland cement paste.

INTRODUCTION

In the last few decades, considerable research effort has been spent on the utilization of industrial by-products (fly ash, blast-furnace slag, microsilica, etc.) and natural resources (limestone, pozzolan, etc.) as partial replacement of Portland cement. The benefits of addition of supplementary materials to Portland cement are well documented [1, 2]. During 1990s, the use of blended cements made with Portland cement and two additions, called ternary or composite cements, has grown and it has been reported that ternary blended cements could substantially improve the performance of concrete compared with the conventional binary blends or regular Portland cement [3,4]. Proper replacement of Portland cement by two suitable supplementary cementing materials can result in not only economical and ecological benefits, but technical benefits as well. Selection of suitable admixtures, proper mixture proportioning and curing technique can greatly improve the properties or durability of concrete compared with the conventional binary blended cements or regular Portland cement. For example, a very low heat of hydration ternary blended cement consisting of Portland cement, granulated blast furnace slag, and fly ash was developed in Japan for mass concrete construction [5]. Considering this ternary blended cement as a slag cement incorporating fly ash, addition of fly ash can increase workability and reduce bleeding of slag cement concrete.

It is also well established that mineral additives may reduce early strength of concrete, especially at relatively high cement replacement rates [6,7,8]. It is attempted to compensate the loss of early strength by different techniques including: (1) curing under elevated temperature [9], (2) increasing the fineness of the cement [10,11] (3) using superplasticizers to reduce water to binder ratio, and (4) activating the mix chemically [12,13]. Use of microsilica as one of the additives in ternary blended cements is very beneficial. For example, incorporation of microsilica in slag cement or fly ash cement, the ternary PC–SL–MS (Portland cement, blast-furnace slag, and microsilica) and PC–FA–MS (Portland cement, fly ash, and microsilica) blended cements were developed and commercially manufactured in Canada [14]. In a recent study [15], it has been reported that inclusion of silica fume in binary blends of Portland cement with blast furnace slag and fly ash positively contributes to reduce the permeability of concrete to chloride ions. The densification of the matrix brought about by the pozzolanic reactions of silica fume blocks the pores and results in reducing permeability.

Microsilica is an important pozzolanic additive for Portland cement. Its use in concrete has become widespread in the areas of both high-strength concrete and where durability is of prime concern. The price of microsilica has risen due to the elevation of its status from a waste material to an exotic supplementary cementing material. It is a highly reactive pozzolanic material due not only to its high amorphous silica
content, but also its average particle diameter of 0.1 µm, and therefore its very high specific surface area. In spite of its useful advantages, microsilica suffers from two important disadvantages. Owing to its extreme fineness and large specific surface area, it is perceived to have large water requirement [16]. In addition, particles of microsilica have a high tendency to flocculate in aqueous suspensions. This tendency necessitates the use of dispersing agents when part of Portland cement is replaced with microsilica.

In contrary to microsilica, limestone has no tendency to flocculate in aqueous suspensions and imparts plasticizing effect in fresh Portland cement paste. Limestone powder can also physically improve the denseness of hardened Portland cement paste due to its filling effect. The optimum use of limestone powder as a supplementary material to Portland cement has therefore technical benefits such as improved workability, bleeding control, lower sensitivity to the lack of curing, and a little bit increased early strengths. On the other hand, loss of strength at later ages due to incorporation of limestone has also been reported [17,18,19]. In addition, Portland limestone cement pastes are susceptible to the thaumasite formation, due to sulfate attack. Thaumasite formation requires the transportation of ions like Ca<sup>2+</sup>, CO<sub>3</sub><sup>2-</sup>, SO<sub>4</sub><sup>2-</sup> and sufficient moisture through the hardened cement paste. The use of mineral admixtures that lower the permeability and refine the pore structure of the hardened cement paste may contribute to better performance of mortars and concretes containing limestone [20].

The study of ternary blended cements, therefore, has attained more and more importance during the last decade to formulate cost effective composite cements with suitable properties.

Until now, very few studies have been devoted to the properties and durability of ternary composite cement containing limestone and silica fume [21,22]. The aim of this research is to study the simultaneous positive influences of microsilica and limestone powder, i.e. pozzolanicity and plasticity respectively, on important physicomechanical properties of fresh and hardened Portland cement pastes. A number of ternary mixes comprising of different percentages of limestone powder and microsilica were prepared and studied by determining their relative workability, 50-day compressive strength, water absorption, bulk specific gravity, and volume of permeable pore space. No superplasticizer or dispersing agent was used throughout the experiments.

## EXPERIMENTAL

### Materials

Portland cement of type II ASTM standard (equivalent to Portland cement EN 197-1-CEM I 32.5 R), limestone, and microsilica were used in this work. Limestone was firstly ground in a laboratory ball mill to attain a suitable fine powder. The specific surface area of limestone powder was measured in accordance with ASTM standard C240. Microsilica containing 96.12 % SiO<sub>2</sub> and having a BET specific surface area of 18000 m<sup>2</sup>/kg was prepared from Iranian ferro-alloys industries. The chemical composition and physical properties of the materials are given in Table 1. Proportions of the studied ternary mixes containing different amounts of microsilica and limestone powder are given in Table 2.

### Test procedure

Ternary mixes of Portland cement, limestone powder, and microsilica at given proportions were thoroughly homogenized in a Jar mill containing very few ceramic balls for 20 minutes. Water-to-cement ratio was taken constant at 0.38 for all mixes for possibility of determining the changes in the workability of fresh pastes brought about by the plasticizing effect of limestone powder. Relative workability of freshly prepared pastes was determined using flow table in accordance with ASTM standard C230/C230M-03. The pastes were cast into cubic and cylindrical specimens of 20×20×20 and 50×100 mm in size respectively and the moulds were kept in a bath of more than 95 % relative humidity at 25°C for the first 24 hours. The moulds were then opened and the specimens were stored at the same conditions for

### Table 1. Chemical composition and physical properties of the materials.

<table>
<thead>
<tr>
<th>Chemical Composition</th>
<th>Portland cement [PC]</th>
<th>Limestone [L]</th>
<th>Microsilica [MS]</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>20.80</td>
<td>0.82</td>
<td>96.32</td>
</tr>
<tr>
<td>Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>4.58</td>
<td>0.13</td>
<td>0.84</td>
</tr>
<tr>
<td>Fe&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>3.70</td>
<td>0.12</td>
<td>0.59</td>
</tr>
<tr>
<td>CaO-total</td>
<td>64.46</td>
<td>54.58</td>
<td>0.35</td>
</tr>
<tr>
<td>MgO</td>
<td>2.62</td>
<td>0.79</td>
<td>0.29</td>
</tr>
<tr>
<td>SO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>2.07</td>
<td>0.10</td>
<td>0.10</td>
</tr>
<tr>
<td>K&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>0.52</td>
<td>0.14</td>
<td>0.25</td>
</tr>
<tr>
<td>Na&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>0.15</td>
<td>0.10</td>
<td>0.40</td>
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<tr>
<td>LOI</td>
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<td>CaO-free</td>
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<td>Bogue’s Potential</td>
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<td>Phase Composition</td>
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<td>C&lt;sub&gt;S&lt;/sub&gt;</td>
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<td></td>
<td></td>
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<tr>
<td>C&lt;sub&gt;2&lt;/sub&gt;S</td>
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<tr>
<td>C&lt;sub&gt;3&lt;/sub&gt;A</td>
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<td></td>
<td></td>
</tr>
<tr>
<td>C&lt;sub&gt;2&lt;/sub&gt;A&lt;sub&gt;F&lt;/sub&gt;</td>
<td>11.26</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Specific Surface Area (m&lt;sup&gt;2&lt;/sup&gt;/kg) (Blaine)</td>
<td>295 (Blaine)</td>
<td>320 (Blaine)</td>
<td>18000 (BET)</td>
</tr>
<tr>
<td>Density (kg/m&lt;sup&gt;3&lt;/sup&gt;)</td>
<td>3.130</td>
<td>2.750</td>
<td>0.318</td>
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</table>
Simultaneous influences of microsilica and limestone powder on properties of Portland cement paste

Further curing. From each system, three cubic specimens were used for measurement of 50-day compressive strength. The average of the three values was reported as the result of compressive strength measurement. Water absorption, bulk specific gravity, and permeable pore space were determined according to the following procedure and using cylindrical paste specimens.

a) Specimens were weighed and dried in an oven at a temperature of 100 to 110°C for 48 hours. The specimens were then allowed for 5 hours in dry air to cool to the temperature of 25°C and weighed again. This procedure was repeated until the difference between any two successive weights was less than 0.5% of the lowest one. This last weight was designated by A as the oven-dry weight.

b) After final drying, cooling, and weighing, the specimens were immersed in water at 25°C for 72 hours. They were weighed after removing their surface moisture with a towel. This procedure was repeated until the difference between any two successive weights was less than 0.5% of the heavier weight. The final surface-dry weight after immersion was designated by B as the saturated weight after immersion.

c) The specimens were placed in a receptacle, covered with tap water, and were boiled for 5 hours. They were then allowed to cool and their surface moisture was dried with a towel. The soaked, boiled, surface-dried weight was designated by C as the saturated weight after boiling.

d) After immersion and boiling, the specimens were suspended in water at 25°C by a wire and again weighed. This weight was designated by D as the immersed weight.

Using the above determined weights and the following formulas, bulk specific gravity, volume of permeable pore space, and water absorption of specimens were calculated:

- Bulk specific gravity, dry = \[
\frac{A}{(C - D)}
\]

- Volume of permeable pore space, % = \[
\frac{(C - A)}{(C - D)} \times 100
\]

- Water absorption after immersion, % = \[
\frac{(B - A)}{A} \times 100
\]

X-ray diffractometry (JEOL JDX-8030) technique was applied to investigate the mineral phases present in the hardened pastes.

Table 2. Mix proportions of the studied ternary mixes.

<table>
<thead>
<tr>
<th>Limestone (wt.%)</th>
<th>Microsilica (wt.%)</th>
<th>Portland Cement (wt.%)</th>
<th>Limestone (wt.%)</th>
<th>Microsilica (wt.%)</th>
<th>Portland Cement (wt.%)</th>
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<td>30</td>
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</tr>
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</table>

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RESULTS AND DISCUSSION

Paste workability

The results obtained for spread diameter in flow table test as a measure of relative paste workability are presented in Figure 1. The quantitative changes brought about in spread diameter by each of the two supplementary materials individually are also given in table 3. As seen, both microsilica and limestone powder significantly affect the value of the spread diameter or the relative paste workability. The effects however are oppositely. Any partial replacement of cement by microsilica alone significantly lowers the spread diameter of the cement paste due not only to its relatively high capability of water absorption [23], but also to high tendency of its particles to flocculate in aqueous suspensions. Particles of limestone powder however have a quite lower tendency to flocculate in aqueous suspensions and dispersion of which in the cement paste results in a plasticizing effect. As seen in table 3, replacement of cement by limestone powder up to 20 percent by weight of cement increases the spread diameter of the plain cement paste by 4.7%. Higher levels of replacement however have lower plasticizing effects.

In the presence of microsilica, limestone powder affects the paste workability differently. As seen in Figure 1, incorporation of limestone powder to mixes containing relatively lower amounts of microsilica, e.g. 4 and 8 percent by weight of cement, does not significantly affect the paste workability. For mixes containing 12% microsilica however, incorporation of limestone powder at any percentage results in a significant reduction in spread diameter. In ternary mixes therefore, the effect of limestone powder on paste workability depends on microsilica content of the cement paste.

Compressive strength

Results obtained from measurement of 7- and 50-day compressive strengths are presented in Figures 2 and 3. Similar trends are observed in both 7- and 50-day compressive strengths. As seen, partial replacement of cement by limestone powder always decreases...
Simultaneous influences of microsilica and limestone powder on properties of Portland cement paste

the compressive strength, whereas incorporation of microsilica can result in increased strengths. Up to almost 10 percent by weight of cement, any substitution by microsilica, either with or without limestone powder, always shows a considerable increase in both 7- and 50-day compressive strengths.

According to the literature [17,18,19], limestone as a supplementary material can provide positive effects only on early age compressive strengths up to 7 days based mostly on its filling effect. Incorporation of more than 10 wt.% limestone into cement always reduces compressive strengths after 28 days. According to a recent work [24], marked decreases in compressive strength of the hardened cement paste containing more than 10 wt.% limestone after 28 days of hydration is mainly attributed to a sort of pore opening with a slight increase in both total porosity and bulk density.

Microsilica is a highly reactive pozzolanic material. The reaction of microsilica with calcium hydroxide results in the formation of some additional calcium-silicate hydrate as a secondary reaction product. This additional calcium-silicate hydrate could effectively densify the microstructure of the cement paste and therefore strengthen its mechanical behavior [23-26]. Any increase in the replacement percentage of microsilica up to the optimum value, therefore increases 50-day compressive strength due to the formation of additional calcium-silicate hydrate. At percentages higher than optimum value, it is hypothesized that microsilica separates cement grains [23]. Such a separation between cement grains along with water absorption capacity of microsilica could significantly decelerate the cement hydration reactions and hence weakening the 50-day compressive strength.

The interesting conclusion here is that mixes containing 10 % microsilica and 10 % to 15 % limestone powder exhibit almost the same 50-day compressive strengths as the plain cement paste. It is therefore possible to replace Portland cement by a proportioned mixture of microsilica and limestone powder for improving the strength behavior at a constant W/C-ratio and without dispersing agent. It is also possible to produce ternary composite cements containing relatively high contents of microsilica and limestone powder with no considerable loss in both workability and 50-day compressive strength compared to plain cement paste.

### Table 4. Effects of microsilica and limestone powder on volume of permeable pore space individually.

<table>
<thead>
<tr>
<th>Microsilica (wt.%)</th>
<th>Change in volume of permeable pore space (%)</th>
<th>Limestone Powder (wt.%)</th>
<th>Change in volume of permeable pore space (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>+6.2</td>
<td>10</td>
<td>+1.2</td>
</tr>
<tr>
<td>8</td>
<td>+7.6</td>
<td>15</td>
<td>+1.3</td>
</tr>
<tr>
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<td>+12</td>
<td>20</td>
<td>+3.4</td>
</tr>
<tr>
<td>16</td>
<td>+12.4</td>
<td>25</td>
<td>+9.4</td>
</tr>
</tbody>
</table>

![Figure 4. Volume of permeable space of cement pastes containing different proportions of microsilica and limestone powder.](image)

![Figure 5. Graphical representation of dry bulk specific gravity.](image)

Volume of permeable pore space

The results obtained for dry bulk specific gravity of the hardened cement pastes are presented graphically in Figure 5. As seen, limestone powder and microsilica always result in increased dry bulk specific gravities. Both limestone powder and microsilica posses considerably lower dry bulk specific gravities compared to Portland cement. If limestone powder and microsilica cannot effectively behave as a micro-filler and a pozzolanic
submicro-filler, their physical effect in lowering the dry bulk specific gravity of the cement paste is more announced. On the other hand, as seen before both limestone powder and microsilica result in increased volume of permeable pore space. The dry bulk specific gravity of the studied hardened cement pastes therefore decreases because of incorporation of microsilica and limestone powder.

**Water absorption**

Figure 6 represents the results of water absorption. Limestone powder and microsilica both has increased the amount of water absorption of the studied hardened cement pastes. Increased water absorption is due to increased permeable pore space providing more space to be filled by water and increasing the permeability of the hardened cement paste. Substitution of Portland cement by relatively high proportions of limestone powder, 10 wt% and higher, and/or any proportion of microsilica without dispersing agents therefore creates a higher vulnerability to penetrating aggressive media. Such ternary composite cements are not therefore suitable for applications where durability to penetrating aggressive media is an important factor.

**X-ray diffractometry**

Figure 7 shows the results of XRD analysis of some hydrated ternary blended cement with different proportions of limestone powder and microsilica after 28 days of hydration. The results indicated the formation of Ca(OH)$_2$, released from cement hydration. The peaks characterizing limestone, CaCO$_3$, appeared also in the diffraction patterns. The small double peaks at around 2θ angle of 32° belong to the remaining anhydrous cement phases not yet hydrated.
A comparison of the patterns clearly shows the significant decrease in the intensity of Portlandite peaks with microsilica content of the cement. The higher the proportion of microsilica, the lower the intensity of the peaks. This is an evident proof of microsilica and Portlandite resulting in the formation of amorphous calcium silicate hydrates.

CONCLUSIONS

1. Workability of Portland cement pastes containing relatively lower amounts of microsilica, e.g. 4 and 8 percent by weight of cement, does not significantly decrease with incorporation of limestone powder up to almost 20 wt.% by weight of cement. For mixes containing 12 % microsilica, incorporation of limestone powder lowers the paste workability.

2. It is possible to produce ternary composite cements containing relatively high contents of microsilica and limestone powder with no considerable loss in 7- and 50-day compressive strengths compared to plain cement paste.

3. Substitution of Portland cement by relatively high proportions of limestone powder, 10 wt.% and higher, and/or any proportion of microsilica without dispersing agents cannot act as effective fillers and result in increased permeable pore space and water absorption.

References