USE OF NEUTRALISED BAUXITE REFINERY RESIDUE (BAUXSOL™) TO IMPROVE ACID AND SULPHATE RESISTANCE OF CONCRETES IN AGGRESSIVE ENVIRONMENTS

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Abstract
A previous investigation by the authors established that Bauxsol™, an artificially- neutralised bauxite refinery residue, could be used to replace the natural sand as fine aggregate up to 15% by cement mass without detrimentally affecting strength, modulus of elasticity and alkali-aggregate reactivity of concrete. The research reported in this paper has evaluated the influence of Bauxsol™ on sulphate and acid resistances of concrete, where Bauxsol™ was used as fine aggregate at 0%, 5%, 10%, 15% and 20% by cement mass. Test results indicated that there was an improvement in the compressive strength and mass loss of concrete containing 10% Bauxsol™ by cement mass in both sulphate and acidic environments.

1. INTRODUCTION
Bauxsol™ is an artificially neutralised bauxite refinery residue. It consists of a cocktail of very fine-grained minerals which include mainly hematite, boehmite, gibbsite, sodalite, quartz and cancrinitite. Currently, Bauxsol™ is primarily used in environmental management and remediation projects, such as acid neutralisation and metal trapping, arsenate removal from water and phosphate and phenol removal from aqueous solution [1-3]. A recent investigation [4] carried out by the authors has indicated that Bauxsol™ could be used to replace some part of natural sand in concrete.

The deterioration of concrete in sulphate and acidic environments has been reported worldwide [5-9]. Sulphate attack refers to the deterioration of concrete resulting from the chemical reactions occurring when concrete is exposed to a solution containing a sufficiently high concentration of dissolved sulphates [10]. This is particularly prevalent in arid regions where naturally occurring sulphate minerals are present in water and groundwater. The essence of sulphate attack is the formation of calcium sulphate (gypsum) and calcium sulpho-aluminate (ettringite). Both products occupy a greater volume than the compounds which they replace and, therefore, the expansion of the hardened concrete occurs [11, 12]. Whilst determining the effect of sulphate attack, researchers have often focused on the effect of SO₄²⁻ without equal attention to the cations associated with them. It is now known that concretes, which are considered to be
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resistant to sodium sulphate (Na₂SO₄) attack can be detrimentally affected when exposed to magnesium sulphate (MgSO₄) [13]. Moreover, the intensity and rate of attack also depend on the concentration of the sulphate solution [14].

Hydrated cement paste is an alkaline material and can be attacked by acidic solutions very easily. The severity of the attack depends on the type of acid and the level of acidity, whether weak or strong, depending on the pH of the solution. In industrial environments, the most common acid to attack concrete is sulphuric acid. Therefore, 1% H₂SO₄ solution has been used in many laboratory tests to investigate the acid resistance of concrete for sewer structures [15, 16]. The effect of sulphuric acid attack is the dissolution of the hydrated cement paste resulting in a soft and very weak mass [12].

The use of various supplementary cementitious materials, such as fly ash, silica fume and metakaolin, in concrete has been found to improve the resistance of concrete to both sulphate and sulphuric acid attack [17-21]. The results of an investigation on the effects of Bauxsol™ on sulphate and sulphuric acid resistances are reported in this paper.

2. EXPERIMENTAL PROGRAMME

2.1 Materials

Class 42.5N Portland cement supplied by Blue Circle, complying with BS EN 197-1:2000 [22] as a CEM I material, was used in this study. The coarse aggregate used was crushed basalt with 20mm and 10mm size fractions mixed in the ratio 2:1 by mass and the fine aggregate used was medium graded natural sand complying with BS EN 12620: 2002 [23]. Both materials were obtained from local sources in Northern Ireland. Bauxsol™ was produced at Portoscuso, Sardinia, Italy.

Particle size distributions of the OPC, the Bauxsol™, and the natural sand are presented in Fig. 1. This figure shows that the Bauxsol™ particles have a size distribution much finer than that of the natural sand. It can also be observed that 95% of the Bauxsol™ particles are <10µm and finer than that of the OPC. The chemical composition, determined by X-ray fluorescence (XRF) spectroscopy, of the OPC and the Bauxsol™ is shown in Table 1 and it indicates that Bauxsol™ contains six major constituents, namely Fe₂O₃, Al₂O₃, SiO₂, TiO₂, Na₂O and CaO. The X-ray diffraction (XRD) pattern of Bauxsol™ is presented in Fig. 2, which highlights that the mineralogy of the Bauxsol™ is dominated by hematite and some silicates and aluminium oxy-hydroxide, with minor TiO₂ (rutile and anatase).
Table 1: Chemical composition of OPC and Bauxsol™

<table>
<thead>
<tr>
<th>Oxides (%)</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>MgO</th>
<th>CaO</th>
<th>Na₂O</th>
<th>K₂O</th>
<th>TiO₂</th>
<th>SO₃</th>
<th>P₂O₅</th>
<th>LOI¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>OPC</td>
<td>21.41</td>
<td>5.11</td>
<td>2.61</td>
<td>1.78</td>
<td>61.5</td>
<td>0.33</td>
<td>0.61</td>
<td>--</td>
<td>3.03</td>
<td>0.16</td>
<td>2.58</td>
</tr>
<tr>
<td>Bauxsol™</td>
<td>24.06</td>
<td>20.01</td>
<td>29.60</td>
<td>0.95</td>
<td>2.64</td>
<td>7.45</td>
<td>0.68</td>
<td>5.81</td>
<td>0.90</td>
<td>0.14</td>
<td>7.81</td>
</tr>
</tbody>
</table>

¹LOI- Loss of ignition

Fig. 1: Particle size distributions of OPC, Bauxsol™ and natural sand

Fig. 2: XRD pattern of Bauxsol™
2.2 Mix proportions
The mix proportions for preparing concrete for both the sulphate and sulphuric acid resistances test are summarised in Table 2.

Table 2: Mix proportions

<table>
<thead>
<tr>
<th>Mix ID</th>
<th>OPC (kg/m³)</th>
<th>Water (kg/m³)</th>
<th>Bauxsol™ (kg/m³)</th>
<th>Natural sand (kg/m³)</th>
<th>Coarse aggregate (kg/m³)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>10mm 20mm</td>
</tr>
<tr>
<td>BX0</td>
<td>400</td>
<td>220</td>
<td>0</td>
<td>700</td>
<td>360 720</td>
</tr>
<tr>
<td>BX5</td>
<td>400</td>
<td>220</td>
<td>20</td>
<td>680</td>
<td>360 720</td>
</tr>
<tr>
<td>BX10</td>
<td>400</td>
<td>220</td>
<td>40</td>
<td>660</td>
<td>360 720</td>
</tr>
<tr>
<td>BX15</td>
<td>400</td>
<td>220</td>
<td>60</td>
<td>640</td>
<td>360 720</td>
</tr>
<tr>
<td>BX20</td>
<td>400</td>
<td>220</td>
<td>80</td>
<td>620</td>
<td>360 720</td>
</tr>
</tbody>
</table>

2.3 Manufacture and conditioning test specimens
Nine 100mm concrete cubes were manufactured for each of the mix (Table 2). The cubes were cast by filling the moulds in approximately two equal layers and compacting each layer using a vibrating table. The concrete was considered to be fully compacted when air bubbles stopped appearing on the surface. After the second layer was compacted the specimens were finished lightly with a metal float. The cubes in their mould were covered with a plastic sheet and kept in the casting room at 20(±1) °C for 24 hours. These were then demoulded and transferred to a water bath maintained at 20(±1) °C for curing them in water. After two-days of water curing the specimens were wrapped in polythene sheet and kept in an environmental chamber at 20(±1) °C and 40(±1)% RH, for a period of 25 days.

3. TEST METHODS
The compressive strength of 100mm size concrete cubes which were exposed to the sulphate solutions (10% Na₂SO₄ and 10% MgSO₄) was determined by crushing three of them after a period of 56 and 180 days. The compressive strength of 100mm size concrete cubes after exposing them in 1% H₂SO₄ solution was determined by crushing three of them after the same period of duration. The mass loss of concrete cubes in sulphate solution (10% Na₂SO₄ and 10% MgSO₄) and 1% H₂SO₄ solution was determined by determining the mass of three 100mm cubes exposed for a period of 180 days.

4. RESULTS AND DISCUSSION
4.1 Sulphate resistance
Figures 3 and 4 show the compressive strength of 100mm concrete cubes immersed in 10% Na₂SO₄ and 10% MgSO₄ respectively for 56 and 180 days. In both the cases the compressive strength was marginally the highest for the mixes containing 10% Bauxsol™ content. This improved behaviour could be due to the micro-filler effect of Bauxsol™. However, beyond 10%
replacement level, probably the quantity was more than that required to fill the pores and, the excess Bauxsol™ might have resulted in a reduction in compressive strength.

![Graph showing compressive strength of concrete cubes immersed in 10% Na₂SO₄ and 10% MgSO₄.](image1)

Fig. 3: Compressive strength of 100mm concrete cubes immersed in 10% Na₂SO₄

![Graph showing compressive strength of concrete cubes immersed in 10% Na₂SO₄ and 10% MgSO₄.](image2)

Fig. 4: Compressive strength of 100mm concrete cubes immersed in 10% MgSO₄

Figures 5 and 6 show the mass loss of 100mm concrete cubes immersed for 180 days in 10% Na₂SO₄ and 10% MgSO₄ respectively, which suggest that the mass loss increased for the mix containing 5% Bauxsol™ and then this was the minimum for the mix containing 10% Bauxsol™. However, beyond 10% Bauxsol™, there was again an increase in the mass loss. In order to identify the reasons for the improvement for a 10% replacement level, further investigation is in progress to analyse the chemical phases in the cement paste after the sulphate exposure.
Although MgSO\(_4\) attack is more destructive to concrete than Na\(_2\)SO\(_4\) attack [24, 25], an important point in Figs. 5 and 6 is that the concrete containing Bauxsol™ showed better resistance to 10% MgSO\(_4\) than 10% Na\(_2\)SO\(_4\). This is due to the different mechanisms of the sulphate attack. In Na\(_2\)SO\(_4\) solutions, the deterioration is the result of expansion associated with ettringite formation, whilst in MgSO\(_4\) solutions the main cause of attack is decomposition of C–S–H to M–S–H.

### 4.4 Acid resistance

Figure 7 shows the compressive strength of 100mm concrete cubes immersed for 56 and 180 days in 1% H\(_2\)SO\(_4\). In both the cases, it can be seen that the compressive strength was marginally the highest for the mixes containing 10 to 15% Bauxsol™ content. The mass loss of 100mm concrete cubes immersed for 180 days in 1% H\(_2\)SO\(_4\), as shown in Fig. 8, suggests that there was a reduction in the mass loss for concrete containing natural sand replaced with the Bauxsol™ up to 10% by mass of cement. By combining both these sets of results, it can be concluded that there is an improvement in sulphuric acid attack resistance up to 10% addition of Bauxsol™. The surface degradation of 100mm concrete cubes immersed for 180 days in 1% H\(_2\)SO\(_4\) is shown in Fig. 9. This figure also shows that concrete containing 10% Bauxsol™ behaved in a better way compared to the other mixes.
From the published literature [1, 2], it can be seen that Bauxsol™ has got an excellent capacity to neutralise the acid and trap trace metals. This is believed to be due to the presence of large quantities of acid neutralising carbonate and hydroxy-carbonate minerals, as well as finely crystalline minerals that form weak bases. Therefore, the improved behaviour of concrete in 1% H$_2$SO$_4$ with 10% Bauxsol™ content may be ascribed to the chemical role of acid neutralising/consuming capacity of Bauxsol™.

5. CONCLUSIONS

On the basis of the results obtained in this study, where the natural sand was replaced with the Bauxsol™ by cement mass, it can be concluded that the use of Bauxsol™ up to 10% would improve both the sulphate resistance and the sulphuric acid resistance of concrete. To identify the reasons for the improvement in both compressive strength and reduced mass loss of mixes containing up to 10% Bauxsol™ replacement levels when exposed to sulphate and acidic solutions, further investigations are currently in progress.

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REFERENCES