ABSTRACT

It was well recognized for many years the beneficial utilization of some industrial by-products in improving the properties of fresh and hardened concrete. By-products such as pulverised fuel ash, silica fume and ground granulated blast furnace slag (ggbfs) are added in different proportions to concrete mixtures as either a partial substitute to Portland cement or as admixtures. Concrete prepared with such materials offers improved properties such as better workability, good strength, and enhanced durability compared to normal concrete and has been used in the construction of power and chemical plants and under-water structures. Copper slag (CS), Cement By-pass Dust (CBPD), also known as Cement Kiln Dust, Spent Catalyst (SC), and Ferrochrome Slag (FeCr) are industrial by-product materials produced from the process of manufacturing copper and Portland cement, in oil refinery’s processes, and chrome production, respectively. In Oman, large quantities of copper slag (60,000 tons/year), cement by-pass dust (25,000 tons/year), spent catalyst (7300 tons/year), and ferrochrome slag (2000 tons/month) are produced every year, most of which is not effectively utilized and disposed on-site without any reuse.

This paper presents an overview of the research work conducted to investigate the potential use of different types of industrial by-products such as Copper Slag (CS), Cement By-pass Dust (CBPD), Spent Catalyst (CS), and Ferrochrome Slag (FeCr) in the construction industry in Oman. The effect of these materials on the properties of fresh and hardened concrete and mortars when used as partial replacement of sand or cement is discussed. Laboratory data generally indicate that these materials have good potential to be used as an alternative to the conventional cement and/or aggregate in cement mortars and concrete provided that economic incentives and environmental concerns are taken into consideration.

KEYWORDS: Industrial By-Products, Copper Slag, Cement By-pass Dust, Spent catalyst, Ferrochrome Slag, Concrete, Strength, Durability

1 INTRODUCTION

The best strategy for solid waste management is to work towards achieving the 5Rs of reduction, recovery, recycling, reuse, and research (Su et al., 2001). Industrial By-products generated from different industries are creating environmental problems associated with disposal and pollution. However, such materials can be used in manufacturing fireproof materials, used in concrete as
partial substitutes for cement and/or aggregates or they can be added to clay and heat-treated to produce building materials such as ceramic tiles, and refractory and insulation bricks. Many industrial by-products have pozzolanic properties which qualify them as a viable material which can be used in construction as a substitute for cement or aggregate or they can be used as additives in concrete mixtures. The use of some waste materials such as pulverised fuel ash, silica fume and ground granulated blast furnace slag (ggbfs) in concrete has been well documented in the design specifications (Shi et al. 2008). Concrete prepared with such materials offers improved properties such as better workability, good strength, and enhanced durability compared to conventional concrete and has been used in the construction of important structures such as power and chemical plants and under-water facilities.

The generated industrial by-products in Oman have increased substantially in the last two decades due to the rapid development in the infrastructure and industrial projects as well as the construction of many chemical plants and oil refineries. Accumulation and lack of proper disposal management strategies of such materials are posing environmental, pollution and health problems. Copper slag (CS), Cement By-pass Dust, CBPD, (also called Cement Kiln Dust), Spent Catalyst (SC), and Ferrochrome Slag (FeCr) are industrial by-products produced from the process of manufacturing copper and Portland cement, in oil refinery’s processes, and chrome production, respectively. In Oman, large quantities of copper slag (60,000 tons/year), cement by-pass dust (25,000 tons/year), spent catalyst (7300 tons/year) and ferrochrome slag (2000 tons/month) are produced, most of which are not effectively utilized and disposed on-site without any further reuse.

This paper presents an overview on the research work conducted at Sultan Qaboos University, Oman to investigate the potential use of these industrial by-products in the construction industry in Oman. The effect of using these materials on the properties of concrete and cement-based composites when used as partial replacement of aggregates or cement is presented and discussed.

2 MATERIALS’ CHARACTERIZATION

Different tests were conducted to determine physical properties and chemical composition of ordinary Portland cement (OPC), copper slag, cement by-pass dust (CPBD), and spent catalyst from Sohar refinery (SR) as shown in Tables 1 and 2, respectively (Al-Jabri et al. 2002, Taha et al. 2004, Al-Jabri et al. 2013a). The results shown in Table 1 indicate that CPBD has the highest fineness (i.e. surface area), which is advantageous when considering using such material as a cementitious material, but at the same time it will demand a higher water content whereas copper slag has the lowest fineness which is a characteristic of a low surface area. However, the surface area of spent catalyst is similar to the surface area of ordinary Portland cement. Copper slag has the highest specific gravity of 3.45 while CPBD and spent catalyst has the lowest values of 2.7 and 2.6, respectively. Table 1 also shows that the initial setting time for copper slag and spent catalyst powder alone is delayed by more than double the time of the initial setting determined for OPC, while the initial setting time for CPBD is delayed by approximately 40 minutes. This is primarily due to the low CaO content (6.1% and 0.05%) present in copper slag and spent catalyst, respectively while CBPD is characterized by high free and combined CaO content (63.8%). CaO is known to contribute considerably to the hydration phenomenon of Portland cement. Other studies showed that the specific gravity of the FeCr slag ranges between 2.84 and 3.01 whereas the water absorption ranges between 0.25% and 2.3% (Yılmaz and Karaşahin 2013, Acharya and Patro 2016).
Table 1: Physical properties of ordinary Portland cement, copper slag, cement by-pass dust, and spent catalyst

<table>
<thead>
<tr>
<th>Material Test Type</th>
<th>Ordinary Portland Cement</th>
<th>Copper slag</th>
<th>Cement by-pass dust</th>
<th>Spent catalyst Sohar</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fineness (cm²/g)</td>
<td>3,357</td>
<td>1,261</td>
<td>4,824</td>
<td>≅ 3,500</td>
</tr>
<tr>
<td>Specific gravity</td>
<td>3.15</td>
<td>3.45</td>
<td>2.4</td>
<td>2.6</td>
</tr>
<tr>
<td>Initial setting (minutes)</td>
<td>110</td>
<td>250</td>
<td>150</td>
<td>250</td>
</tr>
</tbody>
</table>

Chemical analyses of CS, OPC, CBPD, SC, and FeCr are presented in Table 2. It can be seen from Table 2 that free and combined limes contribute to nearly 63% of the chemical composition of OPC and CBPD, respectively whereas copper slag, spent catalyst and ferrochrome slag have a very low lime content of approximately 6%, 0.06%, and 3.37% respectively. This indicates that these by-products are not chemically very reactive materials to be used as a cementitious material since sufficient quantity of lime must be available in order to reach the required rate of hydration and to achieve the required early age strength. Therefore, in this case, it would be more beneficial if CS, SC, and FeCr could be chemically activated using lime or CBPD in order to increase its pozzolanic activity.

Table 2: Chemical Composition of ordinary Portland cement, copper slag, cement by-pass dust, spent catalyst and ferrochrome slag.

<table>
<thead>
<tr>
<th>Component</th>
<th>OPC (%)</th>
<th>CS (%)</th>
<th>CBPD (%)</th>
<th>SC– Sohar (%)</th>
<th>FeCr (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>20.85</td>
<td>33.05</td>
<td>15.84</td>
<td>39.21</td>
<td>34.90</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>4.78</td>
<td>2.79</td>
<td>3.57</td>
<td>37.68</td>
<td>23.60</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>3.51</td>
<td>53.45</td>
<td>2.76</td>
<td>0.66</td>
<td>3.72</td>
</tr>
<tr>
<td>CaO</td>
<td>63.06</td>
<td>6.06</td>
<td>63.76</td>
<td>0.05</td>
<td>3.37</td>
</tr>
<tr>
<td>MgO</td>
<td>2.32</td>
<td>1.56</td>
<td>1.93</td>
<td>0.26</td>
<td>22.40</td>
</tr>
<tr>
<td>SO₃</td>
<td>2.48</td>
<td>1.89</td>
<td>1.65</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.55</td>
<td>0.61</td>
<td>2.99</td>
<td>0.06</td>
<td>-</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.24</td>
<td>0.28</td>
<td>0.33</td>
<td>0.43</td>
<td>-</td>
</tr>
<tr>
<td>Loss on ignition</td>
<td>1.75</td>
<td>0</td>
<td>5.38</td>
<td>2.43</td>
<td>-</td>
</tr>
<tr>
<td>Al₂O₃ + SiO₂ + Fe₂O₃</td>
<td>29.14</td>
<td>89.29</td>
<td>22.17</td>
<td>77.55</td>
<td>62.22</td>
</tr>
</tbody>
</table>

OPC: Ordinary Portland Cement, CS: Copper slag, CBPD: Cement By-pass Dust, SC: Spent Catalyst, FeCr: Ferrochrome Slag

On the other hand, CD and SC have high concentrations of SiO₂ and Fe₂O₃ compared with OPC and CBPD. In comparison with the chemical composition of natural pozzolans of ASTM C618-99, the summation of the three oxides (SiO₂+Fe₂O₃+Al₂O₃) in CS and SC is nearly 89% and 78%, respectively, which exceeds the 70% percentile requirement for Class N raw and calcined natural pozzolans whereas FeCr has a summation value of 62% which means that it has low
pozzolanic activity. From the material characterization tests, it seems that CS and FeCr are more suitable as an aggregate substitute in concrete than cement replacement. Also, leachate tests showed that mixtures prepared using SC and FeCr contained small traces of heavy metals that are far below the international limits (Al-Jabri et al. 2013a, Acharya and Patro 2016). Hence, no environmental harm should be anticipated from the use of both materials in construction.

3 USE OF COPPER SLAG AS A CEMENTITIOUS MATERIAL

Experimental studies (Al-Jabri et al. 2002, Al-Jabri et al. 2006, Al-Jabri et al. 2009a, Al-Jabri et al. 2009b, Al-Jabri et al. 2011) were conducted to study the effect of using copper slag as a cementitious material on the properties of cement mortars, normal concrete, and high strength concrete. Figure 1 shows the effects of copper slag addition as cement replacement on the strength of cement mortars. It shows that there is a reduction in the compressive strength of the cement mortars as the copper slag content increases. The optimum copper slag to be used as cement replacement is 5%.

![Figure 1: Effect of copper slag on the compressive strength of cement mortars](image)

An experimental testing program was carried out to investigate the effect of copper slag and cement by-pass dust addition as cement replacement on concrete properties (Al-Jabri et al., 2006). In addition to the control mixture (mixture 1), two different trial mixtures were prepared using different proportions of copper slag and cement by-pass dust. CBPD was primarily used as an activator. Mixture 2 consisted of 5% copper slag substitution for OPC whereas Mixture 3 consisted of 13.5% copper slag, 1.5% cement by-pass dust and 85% OPC. Three water-to-binder (w/b) ratios were studied: 0.5, 0.6 and 0.7. Concrete cubes, cylinders and prisms were prepared and tested for strength after 7 and 28 days of curing. The modulus of elasticity of these mixtures was also evaluated. Results presented in Figure 2 show that 5% copper slag substitution for Portland cement gives a similar strength performance as the control mixture, especially at low w/b ratios (0.5 and 0.6). Higher copper slag (13.5%) replacement yielded lower strength values.
The results also demonstrated that the use of copper slag and cement by-pass dust as partial replacements of OPC has no significant effect on the modulus of elasticity of concrete, especially at small quantities substitution.

Concrete mixtures made of copper slag as a substitution for sand showed an increase in the workability with the increase of copper slag percentage in concrete which resulted in a decrease in the compressive strength of both normal and high strength concrete (Al-Jabri et al. 2009a, Al-Jabri et al. 2009b, Al-Jabri et al. 2011) because copper slag particles has much lower water absorption (0.17%) than sand (1.36). This suggests that copper slag would demand less water than that required by sand in the concrete mix. Therefore it is expected that the free water content in concrete matrix will increase as the copper slag content increases which consequently will lead to an increase in the workability of the concrete.

To study the effects of copper slag on the properties of normal and high strength concrete when used in lieu of sand, various mortar and concrete mixtures were prepared with different proportions of copper slag ranging from 0% (for the control mixture) to 100% as fine aggregates replacement. Cement mortar mixtures were evaluated for compressive strength, whereas concrete mixtures were evaluated for workability, density, compressive strength, tensile strength, flexural strength and durability. The results obtained for cement mortars revealed that all mixtures with different copper slag proportions yielded comparable or higher compressive strength than that of the control mixture. Also, there was more than 70% improvement in the compressive strength of mortars with 50% copper slag substitution in comparison with the control mixture. However, addition of more copper slag resulted in strength reduction due to the increase in the free water content in the mix. Also, the results demonstrated that surface water absorption decreased as copper slag content increases up to 50% replacement. Beyond that, the absorption rate increased rapidly and the percentage volume of the permeable voids was comparable to the control mixture.
Based on these findings it was anticipated that much better results could be achieved if high strength concrete made with copper slag as a fine aggregate is tested at constant workability. Therefore, two series of concrete mixtures were prepared with different proportions of copper slag. The first series consisted of six concrete mixtures prepared with different proportions of copper slag at constant workability. The water content was adjusted in each mixture in order to achieve the same workability as that for the control mixture. Twelve concrete mixtures were prepared in the second series. Only the first mixture was prepared using superplasticizer whereas the other eleven mixtures were prepared without using superplasticizer and with different proportions of copper slag used as sand replacement. The results indicated that addition of up to 50% of copper slag as sand replacement yielded comparable strength with that for the control mix. However, addition of more copper slag causes reduction in the strength due to the increase of the free water content in the mixture as shown in Figure 3. Also, the results demonstrated that the surface water absorption decreased as copper slag quantity increases up to 40% replacement beyond that the absorption rate increases rapidly. At constant workability, there was an almost 22% reduction in the water demand at 100% copper slag replacement in comparison with the control mixture with more than 20% improvement in the compressive strength of concrete. Also, the surface water absorption of high strength concrete for all mixtures was better or comparable to the control mixture.

![Figure 3: Effect of copper slag replacement as a fine aggregate on the workability and compressive strength of high strength concrete](image)

4 USE OF CEMENT BY-PASS DUST IN CONCRETE

Cement by-pass dust (CBPD) contains large quantity of CaO since it's a by-product generated from the manufacturing of cement. Therefore the benefits of using this material as cement replacement or as an activator for other waste material such as copper slag in cement mortars and concrete mixtures were studied by Al-Jabri et al. (2002) and Al-Harthi et al. (2003). Various mortar mixtures were prepared using combinations of sand, water, OPC, CS, CPBD, and lime. A water-to-binder ratio of 0.4 was used. The results showed that the use of CPBD as a partial replacement for OPC (Figure 4) or as an activator for copper slag has resulted in an
improvement in the compressive strength of cement mortars at all curing ages and it would perform better than copper slag in concrete when used as a partial OPC replacement. Also the use of CPBD as an activating agent with copper slag would enhance significantly the compressive strength of cement mortars. The optimum percentage of CPBD was 5%.

![Figure 4: Effect of cement by-pass dust (CBPD) on the compressive strength of cement mortars](image)

The study reported by Al-Harthy et al. (2003) on the use of CBPD in concrete suggested that concrete mixtures containing lower percentages of CBPD (5%) produced close compressive strength, flexural and toughness values to the control mix, especially at a water-to-binder ratio of 0.50. The study also showed that sorptivity of mortar decreased with incorporation of CBPD in the mixtures and without affecting strength, addition of CBPD improves absorption properties of mortars and thus, can enhance their durability.

5 POTENTIAL USE OF SPENT CATALYST AS A CONSTRUCTION MATERIAL

Spent catalyst is a by-product generated by oil refineries. There are two types of spent catalysts produced from oil refineries in Oman; Zeolite catalyst generated at Sohar Refinery (SR) and Equilibrium catalyst generated at Mina Al-Fahl Refinery (MAF). Spent catalyst can be used in concrete applications due to its pozzolanic nature. Studies were conducted to investigate the potential use of spent catalyst as sand or cement replacement in cement mortars (Al-Jabri et al., 2013a), concrete mixtures (Al-Jabri et al., 2013b), and in the production of masonry blocks (Taha et al., 2012).

The effect of using FCC spent catalyst on the compressive strength of mortars was investigated. The main constituents of mortar; sand and cement were partially replaced by different percentages of spent catalyst. Five levels of sand replacement were used ranging from 5% to 25% by weight of sand. The same was done for cement but with different proportions from 2% to 10% by weight of cement. Three water-to-binder ratios were used; 0.50, 0.55 and 0.60 whereas the binder-to-sand ratio was kept constant at 1:3. The specimens were tested at 7, 14,
28, 56 and 91 days of curing. Encouraging results were achieved when Sohar Refinery’s spent catalyst was used as sand replacement. The substitution reached up to 20% without affecting the mortars’ compressive strength. Spent catalysts from both refineries showed negligible effect on the strength of cement mortars when used as partial substitute of cement as shown in Figure 5.

Figure 5: Effect of using spent catalyst from Sohar refinery as cement replacement in cement mortars at 28 days

Figure 6 shows compressive strength results for masonry blocks prepared with different percentages of spent catalyst as cement replacement. The results indicated that the use of up to 15% spent catalyst as a cement replacement will exceed the minimum compressive strength of 3.5 MPa required in Omani Standard by more than two folds. There was a general fluctuation in the data as the blocks prepared using 15% spent catalyst produced higher compressive strengths that those blocks prepared using 10% spent catalyst. Also, the blocks prepared using 5% spent catalyst had equal or better compressive strength than those of the control blocks (0% spent catalyst).

Figure 6: Compressive strength results for masonry blocks prepared with different percentages of spent catalyst
Concrete mixtures with different proportions of spent catalyst were prepared in order to study the potential use of spent catalysts in concrete as partial substitute of sand at w/c ratios of 0.5 and 0.7. They were evaluated for compressive strength, setting time, water absorption, and corrosion resistance. The results showed that using 25% of the Sohar refinery’s spent catalyst as sand replacement gave 73% increase in the cube compressive strength at w/c ratio of 0.7. However, using spent catalyst from Mina Al-Fahl Refinery as sand replacement decreases the compressive strength gradually with the increase of spent catalyst percentage. The results also indicate that the elapsed time decreased as the quantity of spent catalyst from both refineries increases. Negligible increase in the total water absorption was observed in concrete when both spent catalysts were used. Concrete specimens made with spent catalyst from Sohar Refinery showed good corrosion resistance than the control mixture whereas spent catalyst from Mina Al-Fahl Refinery accelerated the corrosion process.

6 APPLICATION OF FERROCHROME SLAG

Ferrochrome slag (FeCr) is a by-product from the production of ferrochrome. Most ferrochrome slags contain a significant amount of heavy metals, the release of which can cause environmental problems. However, there are environmental and economic advantages in seeing slags as a potentially useful resource rather than as waste products. Slag management at ferrochrome producing companies has been influenced by the limited space available and financial cost implications of the slag dumps. Internationally (e.g. South Africa, India, Norway, Turkey, East Europe, China, Sweden and USA), ferrochrome slag is used commercially in the road and construction Industries.

The ferrochrome slag is hard and is chemically very stable and it is well suitable for demanding structures. Slags formed in production of high carbon ferrochrome are usually dumped. Utilization of dumped ferrochrome slag in road construction reduces the cost of product and is friendly to the atmosphere. This material is being used for road construction, brick manufacturing and has recently been tried in cement industry and as a base layer material in road pavements due to its excellent technical properties. Slags have been used in pavement construction as engineering fill, subbase and base, ferrochrome slag was used as a hardener in the development of a fire proof concrete. It is a good alternative to using the quarry material of primary. There are environmental and economic advantages in seeing slags as a potentially useful resource rather than as waste products. In many cases, valuable metals can be recovered from slags, and the slag can be rendered inert thereby making it available as a construction material.

Yilmaz and Karaşahin (2013) used FeCr slag as stabilized base material with Portland cement content in the range of 2 to 10%. The study found that a percentage of 4% or higher met the compressive strength standards (Figure 7). Leaching tests were conducted according to the Synthetic Precipitation Leaching Procedure (SPLP). Results showed that only Cr content was significant as heavy element, but met the US EPA limits of concentration. Das (2014) presented the material characterization of FeCr slag. In terms of oxides, it contained mainly aluminum, silicon, magnesium and chromium oxides. FeCr slag was divided into coarse and fine slags. Evaluation of the material was done for use as an embankment and granular subbase. The study provided data for compaction, soundness and CBR results for the FeCr slag. Niemela and Kauppi (2007) reported on the production of FeCr slag in Finland. Slag is used in road and civil construction. Leaching was low and performance results were excellent. Slag products were
used successfully to replace natural sand. Leaching tests from column test carried out in Finland indicated low leaching of chrome.

![Compressive strength results of FeCr samples after 28 days of curing (Yilmaz and Karaşahin 2013).](image)

In a recent study, Acharya and Patro (2016) studied the effect of using ferrochrome ash (FCA) and lime dust in concrete properties. Up to 40% of FCA was used as cement substitution in concrete mixtures in four different substitutions at an interval of 10%. FCA was modified with lime dust to enhance the performance of concrete in which substitution of lime was considered as 7% after studying its effect on blended cement based concrete. The results from Acharya and Patro study indicated that replacement of OPC up to 47% by FCA (40%) and lime dust (7%) has comparable positive impact on the 28 days strength and appreciable impact on long term strength properties.

Studies presented in the literature on the potential use of ferrochrome slag concluded that such material possesses good mechanical properties and durability which makes it good choice to be utilized in pavement construction as engineering fill, subbase and base and as an aggregate in concrete mixtures.

7 CONCLUSIONS

Different industrial by-product materials are produced in Oman. Such materials include copper slag, cement by-pass dust, spent catalyst, and ferrochrome slag. Recycling of such materials in building construction is not practiced. Promising laboratory results indicate that the potential reuse of such by-products as cementitious materials in the production of concrete and masonry blocks which possess good mechanical properties and durability that is comparable to the conventional concrete. The production of industrial by-products in Oman is expected to increase rapidly in the coming few years due to the industrial development in the country which will have a detrimental impact on the environment unless waste management policies and legislations are developed. Successful utilization of industrial by-products in the construction industry would
require more detailed economic and environmental analyses as well as engineering design specifications.

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