TRACE ELEMENTS CONCENTRATION IN VARIOUS BRANDS OF PORTLAND CEMENT IN PAKISTAN AND THEIR EFFECTS ON THE QUALITY OF CEMENTS: A COMPARATIVE STUDY

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ABSTRACT
Trace elements occur naturally in Portland cement in very minute quantity; they mainly come from the raw materials and fuel used during the manufacturing process. They are entering to various mineral phases of Portland cement and affect the clinker grindability, initial and final strength as well as the setting time. Some trace metals are also responsible for characteristic colour to cement. In order to know the effect of trace metals in various brands of Portland cements in Pakistan, seven brands of Portland cement were collected from Peshawar and Jahangira (Swabi) which were analyzed by using Atomic absorption spectrometric techniques. As a result six trace elements were determined in the samples namely; Chromium (Cr), Nickel (Ni), Cadmium (Cd), Copper (Cu), Cobalt (Co) and Zinc (Zn), and their comparative quantification in various brands of Portland cements and their effect on the quality of the relevant cement has been discussed.

Keywords: Portland cement, Trace Elements concentration, effect on the quality of cement.

1. INTRODUCTION
Portland cements are prepared by heating mixtures of limestone and clay, or other materials at ~1450°C. This results in the formation of clinker by Partial fusion which is then mixed with a few percentage of calcium sulfate in the form of gypsum and finally mixed and ground to fine powder, and hence cement is produced. Calcium sulfate controls the rate of set and influences the rate of strength development. The composition of clinker is 67% CaO, 22% SiO2, 5% Al2O3, 3% Fe2O3 and 3% other components, and contains normally four major phases, called alite, belite, aluminate and ferrite. The trace elements are defined in different ways such as the elements occurring at less than 0.02% are regarded as trace elements whereas some argue that if the quantity of elements present is less than 100 ppm are regarded as trace elements. Despite their very small quantity, trace elements greatly affect the manufacturing quality of Portland cement, such as the grindability of clinker, strength and setting time. On the other hand, they affect the fuel consumption during the manufacturing process. Trace elements in Portland cement come from a variety of sources, such as clay/shale, iron ore, bauxite and coke (raw materials), coal, used oils and tires (fuel). The presence of about 17 trace elements namely; antimony, arsenic, lead, cadmium, chromium, cobalt, copper,
manganese, nickel, thallium, tin, vanadium, zinc, beryllium, selenium, tellurium and mercury has been reported in cement kiln dust. Previously work was initiated on the origin of the major, minor and trace elements in cement and their effect on the quality of cement and their affinity for mineral phases during clinker formation and its grindability. It is also reported that the trace elements like Cd, Pb, Cr and Zn are entering in large concentration to Portland cement and calcium aluminate cements from the raw materials and affect the manufacturing qualities of cement. Such as addition of Cd and Zn in large quantity to Portland cement increase the setting time and negatively affect the strength of the cement; however, unlike Cd and Zn, chromium addition decreases setting time and increases strength. Similarly calcium aluminates cements easily catch Cd and Cr which is responsible for delayed setting time and good strength and Pb with normal setting time and strengths, Large quantity of zinc oxide has toxic effects on calcium aluminate strength. During clinker formation, trace elements like Cr, Zn, Ba, Ni, Ti and P form solid solution with silicate mineral phases i.e. alite & belite, which is responsible for decreasing hardness of the clinker.

According to the Asian Development Bank report (2008), the cement industry in Pakistan has come a long way since establishment. With 10 million tons per annum capacity and 24 operational units it is still growing. The industry is contributing Rs. 30 billion in taxes to the country’s economy. The industry has achieved an overall economic growth of 32% and the demand for cement is believed to have increased by 24%. The overall number of workers working in the construction sector is 2.5 million.

The main aim of this study was to ascertain and compare the concentration of trace elements in various brands of Portland cement in Pakistan and to assess their effects on the quality of cement.

2. MATERIALS AND METHODS
For this study, seven known brands of cement (Askari Cement, Cherat Cement, DG cement, Lucky Cement, Best Way Cement, Kohat Cement and PakCem) of Portland cement were collected from their respective dealers in Jhangira (Swabi) and Peshawar.

The samples were prepared by taking 1g of sample in Teflon beaker. The acid digestion of the samples was done by the following steps:

The sample was subjected to heating for at least 1h after adding 3-5 ml of hydrofluoric (HF) acid.

Then 5-10 ml of Equa-Regia (HNO₃ and HCl in 1:3 ratio) was added to the solution, and the solution was heated using a hot plate in a fume hood until the contents of the Teflon beaker became dry. 20 ml of 2N HCl was added to the contents of the Teflon beaker and heated for a while. The contents were then diluted to 50 ml, using de-ionized water.

The solution was then used to analyze six trace metals namely, Cr, Ni, Co, Zn, Cu and Cd using Perkin Elmer 700 AAS, atomic absorption spectrometer (AAS) in the Geochemistry laboratory of the National Centre of Excellence in Geology, University of Peshawar.

3. RESULTS AND DISCUSSION
Table 1 summarizes the concentrations of various trace elements detected in the selected samples of the Portland cement studied. Table 2 gives a comparison of the normal average concentration of the trace elements reported
internationally, the trace elements in the raw materials used in the manufacturing of the Portland cement in Pakistan and those observed in the present study. It is evident from Table 1 that the average concentration of chromium is greater (8 ppm) than the average standard concentration reported internationally. The highest concentration of Cr was found in Pak cement followed by Lucky cement. Chromium concentrations in the various brands follow the sequence (in decreasing order): Pak Cement > Lucky > DG > Best way = Kohat > Askari > Cherat.

Table 1. Comparative analysis of trace elements in the samples of Portland cement.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Cr (ppm)</th>
<th>Ni (ppm)</th>
<th>Cd (ppm)</th>
<th>Cu (ppm)</th>
<th>Co (ppm)</th>
<th>Zn (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Askari</td>
<td>38</td>
<td>20</td>
<td>1</td>
<td>10</td>
<td>12</td>
<td>34</td>
</tr>
<tr>
<td>Cherat</td>
<td>24</td>
<td>27</td>
<td>&gt;1</td>
<td>20</td>
<td>9</td>
<td>85</td>
</tr>
<tr>
<td>D.G. Khan</td>
<td>53</td>
<td>38</td>
<td>1</td>
<td>16</td>
<td>15</td>
<td>29</td>
</tr>
<tr>
<td>Lucky</td>
<td>58</td>
<td>35</td>
<td>3</td>
<td>11</td>
<td>13</td>
<td>25</td>
</tr>
<tr>
<td>Best way</td>
<td>48</td>
<td>31</td>
<td>3</td>
<td>11</td>
<td>18</td>
<td>25</td>
</tr>
<tr>
<td>Kohat</td>
<td>48</td>
<td>55</td>
<td>3</td>
<td>14</td>
<td>13</td>
<td>29</td>
</tr>
<tr>
<td>Pak Cem</td>
<td>67</td>
<td>45</td>
<td>4</td>
<td>18</td>
<td>27</td>
<td>38</td>
</tr>
</tbody>
</table>

Table 2. Comparison of the average values in normal cement and average values reported in this study.

<table>
<thead>
<tr>
<th>Trace element</th>
<th>Avg value in normal cements</th>
<th>Raw meals</th>
<th>Average value in this Study</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chromium</td>
<td>40</td>
<td>16</td>
<td>48</td>
</tr>
<tr>
<td>Cadmium</td>
<td>0.4</td>
<td>0.34</td>
<td>2.28</td>
</tr>
<tr>
<td>Nickel</td>
<td>24</td>
<td>31</td>
<td>35.85</td>
</tr>
<tr>
<td>Cobalt</td>
<td>10</td>
<td>23</td>
<td>15.28</td>
</tr>
<tr>
<td>Zinc</td>
<td>140</td>
<td>23</td>
<td>37.85</td>
</tr>
<tr>
<td>Copper</td>
<td>25</td>
<td>16</td>
<td>14.28</td>
</tr>
</tbody>
</table>
The presence of Cr in raw materials is responsible for reducing the viscosity of cement clinker melt and goes largely to belite phase of the cement, which depends on the availability of oxygen in cement kiln and ionic charge of Cr, i.e. forming most stable state of Cr$^{+6}$ on high concentration of oxygen and scarcity of oxygen lead to Cr$^{+3}$. Cr$^{+6}$ is readily soluble in water and leads the hydration characteristic of cement paste while Cr$^{+3}$ is less soluble in mix water. It also imparts characteristics colour to cement$^{10}$. It is evident from Table 2 that chromium concentration is significantly higher in the end product which may be due to the use chrome-rich grinding media in the manufacturing processes. The use of chromium alloy balls for grinding of the clinker made the concentration of chromium almost double and accelerated hydration of paste and may be responsible for early strength$^{11}$. The entering of Cr to Portland cement is reported from following the raw material of cement 16 ppm in lime stone, and clay and shale contain ~100 ppm. It is also reported that up to 4% chromium can also enter cement by using chromium bricks$^{12}$. By addition of 0.75% chromium in the form of its salts like nitrate and chloride accelerate paste hydration and responsible for reducing the setting time; however, the early strengths (3 days) are comparatively improved$^{13}$. In the studied samples, the concentration of Cr in PakCem is high followed by Lucky & DG. The grindibality of their clinker will be easily compared to others and ultimately will save the fuel consumption as well as their early strengths (3 days) are comparatively high while their setting time will be reduced respectively.

Nickel concentration is the highest in samples from Kohat cement followed by PakCem. Nickel play an important role in clinker formation. It is mostly concentrated in the ferrite phase, followed by alite, aluminate and belite during mineral phase’s formation. It has been reported that from 0.5 to 1% of Ni can stabilize alite$^{14}$. Table 2 indicates that the concentration of Ni decreases in the end product which may be due to its volatile nature during the cement manufacturing process; however, most of the Ni compounds are non-volatile. The entering of Ni to cement is reported from the raw materials i.e. limestone contains 1.5-7.5 ppm Ni, clay or shale contains 61-71 ppm, coal 20-80 ppm, used oil 3-30 ppm, and petroleum coke 208 ppm$^{12}$. Table 2 shows that Ni concentration in the studied samples is higher than the normal standard concentration. On the basis of Ni concentration, Kohat cement shows the highest concentration followed by PakCem. As a result the initial comparative strength (1-5 days) of Kohat cement is high followed by PakCem and D.G and their clinker grindability will be also easy.

The presence of Zn in Portland cement is responsible for increasing the setting time and decreasing the strength and is reported to be coming from the raw materials i.e. limestone conations 22-24 ppm, clay or shale from 59-115 ppm and coal 16-220 ppm in addition to its primary sources i.e. up to 3,000 ppm reported in used oil$^{10}$. 80-90% Zn in the form of ZnO in raw mix has been reported in clinker$^{15}$. In silicates, half of the zinc is distributed with preference for the formation of alite over belite and the remaining half is preference for the ferrite phase over belite and alite and distributed into the matrix$^{16}$. Zinc in clinker is preferentially retained in ferrite followed by alite, aluminat and belite. ZnO additions accelerate clinker formation$^{6}$. It is also reported that the addition of 1% ZnO in the raw mix decreases free lime considerably which is responsible for lowering the quality of cement; however, when its concentration is increased from 1%.

F. Wali, W. Ali, B. Ahmad, F. Rabbi Khan, S. Khan: Trace elements concentration in ............ 35
it reduces the strength. Table 1 indicates that Zn concentration is high in Cherat cement followed by PakCem and Askari respectively. On the basis of Zn, the setting time of Cherat cement is high followed by PakCem, Askari respectively and their strength decrease respectively.

Table 1 indicates that the average concentration of Cd is higher in the present samples than the normal concentration of Portland cement. On the basis of Cd concentration, the samples can be arranged in the following sequence in decreasing order PakCem > Lucky = Bestway = Kohat >>>D.G = Askari > Cherat. Up to 0.34 ppm of Cd has been reported in ordinary Portland cement. It forms halide or sulfates by reacting with the constituent kiln gas and these halides are readily vaporized at peak kiln temperature; however, the form of Cd incorporating to clinker is not yet known. The concentration of Cd in clinker is known to decrease with increasing chloride input in the kiln. Cd in the form of CdO is reported to increase the burnability of the clinker by lowering the melt temperatures. It is also reported that the addition of high concentrations of CdO retard the cement hydration, but not affecting the strength. Addition of soluble cadmium salts (CdC12) has no clear effect on cement hydration. Cd is not leached from the cement pastes when used as CdO and CdC12 admixtures. On the basis of high Cd concentration in samples PakCem followed by Lucky, Bestway and Kohat etc their setting time and early compressive strength are decreasing respectively; however, their compressive strengths were not affected after 24 hours.

Average concentration of Cobalt in the studied samples was greater than the standard concentration of normal cement. In raw mix, the maximum concentration of cobalt in the form of CoO was 23 ppm. Fly Ash and coal also contain 1.275% Co. In raw mixes mostly, Co is incorporated in clinker. Previous investigations show that Co enters ferrite phase followed by alite and belite phases of the cement. It replaces Fe3+ of the ferrite phase and forms C3A-Co phase which is responsible for the hardness of the clinker. Co somewhat reduces the hydraulic activity of alite. It also gives the characteristic color to the cement. It also increases the water demand and marginally reduces the late strength of cement paste. In the studied samples, the concentration of Co was higher than the international standard (10ppm) except Cherat cement so the its clinker would be hard and more energy will be required for their grindability, and their water demand will be also high and their late strength will be marginally lower.

Table 2 indicates that the average concentration of Cu was lower than the average standard concentration of normal cement. Cu enters cement from various sources i.e. in the form of CuO. 16ppm of Cu is reported in raw mixes, coal fly ash contain up to 13% and in commercial clinker up to 90 ppm is reported. Cu is preferably found in the ferrite phase followed by alite, aluminates, and belite phases. Under oxidizing conditions, Cu in the form of CuO is present in small amount and is responsible for stabilization of alite whereas under reducing conditions, Cu occurs as Cu2O which negatively affects both the alite and belite phase formations. CuO also acts as a flux, by decreasing the melting temperature considerably. It is reported that addition of 1% CuO effectively reduces free lime at much lower melt temperatures and ultimately improves the quality of cement. Oxide of cupper greatly affects the formation of cement mineral phases i.e. CuO accelerates allite phase formation where as Cu2O inhibits it. Soluble copper salts are retarders and give
low heat of hydration\textsuperscript{22, 10}. The average concentration of Cu in the studied samples was lower than the normal standard concentration except PakCem. Its high concentration is responsible for lowering the free lime. Free lime combines with water to form Ca(OH)\textsubscript{2} and increases their bond length and upon dehydration, is responsible for cracks in walls.

Note that the impurities, coming from anywhere, are also important in the use of cements for nuclear waste immobilisation\textsuperscript{24}. The nuclear waste immobilisation is mainly dependent upon the supplementary material of the Portland cement such as fly ash and slag etc. Fly ash increases their internal pH which leads to the formation of the respective hydroxide of the nuclide in the form of precipitation, in the presence of slag reduce the redox potential decrease the solubility of some nuclides.

4. CONCLUSIONS
Trace metals play an important role on the manufacturing qualities of Portland cement. The presence of Cr in raw materials is responsible for reducing the viscosity of cement clinker melt and goes largely to belite phase of the cement and make the clinker grindability easy by reducing the viscosity of clinker as well as improving the initial strength of cement while it reduces the setting time. Similarly the effect of Zn is reverse i.e. it is responsible for increasing the setting time and decreasing the strength of cement. The presence of Cd is responsible for effecting the setting time and early compressive strength; however, the compressive strength was not affected after 24 hours. Cobalt is entering to the ferrite phase followed by alite and belite phases of the cement and it replaces Fe\textsuperscript{3+} of the ferrite phase which is responsible for the hardness of the clinker as result more fuel is required for their grindability. It also increases water demand while it marginally lowers the late strength. Cu in the form of CuO acts as a flux. It decreases the melting temperature considerably. In high concentration, it is responsible for lowering the free lime which combines with water forming Ca (OH)\textsubscript{2} and increases the bond length. Upon dehydration, it is responsible for cracks in walls. Besides improving the qualities of Portland cement Chromium, Nickel, Cadmium and Cobalt are known human carcinogens. Higher concentrations of these trace metals may harm human health both via direct exposure and indirect exposure routes. The authors recommend to pay attention to its environmental and health hazards side.

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