Stabilization of Cobalt By Using Blended Cement Pastes

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Abstract. Stabilization of Cobalt Chloride, a representative of soluble cobalt compounds, with five cements pastes based on either Ordinary Portland Cement (OPC) or blended Portland cement with Granulated Blast Furnace Slag (GBFS) or Metakaolin (MK) were studied. Various mixtures were prepared by using a water/solid ratio (W/S) of 0.28 (by weight). Two ratios of Co ions (2.0 and 3.0% by weight of the solid binder) were used by adding to the mixing water. Hydration characteristics of the different cement pastes were investigated via the examination of chemically combined water content, compressive strength, X-ray diffraction analysis and thermal analysis (DTA/TGA). Leaching of cobalt ions from various hardened cement pastes was examined. The results showed that cobalt chloride retards cement hydration through the formation of plumbate salt. The obtained results of leaching showed a high degree of immobilization of Co ions in the various cement pastes. Moreover, partial replacement of OPC by MK is more efficient than GBFS.

Keywords: Solidification/inertization, stabilization, cement hydration and cobalt chloride
1. Introduction

The hydration process in cements made from raw mixtures containing 2 wt% cobalt oxide, in, Co$_2$O$_3$ was studied. The cement pastes were treated in water for different time intervals. Hydration rate and products were studied by means of X-ray diffraction, differential scanning calorimetry, and thermogravimetric analysis. It is concluded that the added oxides provoke, in general, a retardation of the hydration reactions [1].

Co and Ni uptake by hardened cement paste (HCP) to improve the understanding of immobilization process of heavy metals in cement at the molecular level was investigated. Synchrotron based-techniques (micro X-ray spectroscopy (XAS) and micro X-ray fluorescence (XRF)) were used. For Ni and XRF mapping revealed a highly heterogeneous element distribution as far as the concentration is concerned. The XAS studies showed that Ni(II) forms predominantly layered double hydroxide (LDH) phases. In contrast to Ni, Co was found to be present in the oxidation states II and III. Co(II) is predominately incorporated into newly formed Co(II) hydroxide-like phases (Co(OH)$_2$), Co-LDH or Co-phylllosilicates, whereas Co(III) tends to incorporate into a Co(III)O(OH)-like phase or a Co-phyllosilicate [2].

Heavy metals retarded the precipitation of portlandite due to the reduction of pH resulted from the hydrolysis of heavy metal ions during tricalcium silicate (C$_3$S) hydration. Heavy metals are co-precipitated with calcium as double hydroxide [2,3,9] such as Ca$_2$Cr(OH)$_7$·3H$_2$O, Ca$_2$(OH)$_4$4Cu(OH)$_2$·2H$_2$O, CaZn$_2$(OH)$_6$·2H$_2$O) and CaZn$_2$(OH)$_6$·2H$_2$O) according to the equation:
3CaO·SiO₂+M(OH)₂→Ca₂(OH)₄·M(OH)₂·2H₂O

Where M=Cr, Cu, Zu

Metals form the least soluble hydroxides retard hydration reactions while those that form more soluble hydroxides exhibit only a slight degree of retardation; and metals forming soluble hydroxides behave as accelerators of cement hydration. Retardation has been attributed to the reduction in the permeability caused by these reaction products, that is the precipitation of insoluble metal colloidal gels on cement grain surfaces.

The leaching of heavy metals in the S/S materials can be considered as pH dependent and the corresponding metal hydroxide solubility controlled process. Mineral additions enter the hydration reactions in the mixtures and favor the formation of specific microstructure promoting the immobilization of hazardous elements [6]. High pH is effective in immobilizing many toxic metals, by precipitation and sorption reaction [7]. The leaching behavior of 60Co and 137Cs from spent ion exchange resins in cement-bentonite clay matrix has been studied [8]. From the leaching data the apparent diffusivity of cobalt and cesium in cement–bentonite clay matrix with a waste load of 290–350 kg/m³ the cation exchange resins was measured as ⁶⁰Co: (1.0–4.0) × 10⁻⁶ cm²/d and for ¹³⁷Cs: (0.5–2.6) × 10⁻⁴ cm²/d after 245 days.

The degree of immobilization of the added Co(II) metal ions was evaluated by determining the leached ion concentration after time intervals extended up to 180 days. The leachability experiments were carried out by using two modes: the static and the semi-dynamic
leaching processes. It was noticed that the concentration of the leached Co$^{2+}$ ions in the static mode of leachability was lower than the solubility of hydroxide in all the investigated cement pastes$^{[9]}$.

2. Experimental

2.1. Materials and specimens

The materials used in this investigation were; ordinary Portland cement (OPC), granulated blast furnace slag (GBFS), metakaolin (MK) and cobalt chloride. The chemical analysis of the utilized materials is given in Table 1.

Various cement mixtures were prepared namely; neat Portland Cement (MI), 80%PC+20%GBFS (MII), 60%PC+40%GBFS (MIII), 80%PC+20% MK (MIV) and 60%PC+40%MK (MV).

Two ratios of Cobalt ions were used; 2.0 and 3.0% by weight of the solid binder by adding to the mixing water. The water/solid ratio used was 0.28 for all mixtures. The pastes were moulded in the form of one cubic inch and treated at about 100% relative humidity for the first 7 days. Then the samples were immersed in tap-water for the rest of hydration times which extended up to 90 days.

2.2. Methods of investigation:

The hydration characteristics of the different cement mixes were investigated via; the determination of chemically combined water contents, compressive strength, and phase composition using XRD technique. The degree of immobilization of cobalt ions in the different cement pastes was evaluated through measuring the leached cobalt ions concentration using a static process$^{[10]}$.

3. Results and discussion

3.1. Hydration Characteristics

3.1.1. Combined Water Content (Wn %)
The results of chemically combined water and content are shown in (Fig. 1) for all mixtures in absence and presence of cobalt Chloride. It is obvious that there is a continuous and gradual increase in the combined water contents for all mixtures up to 90 days. This increase may be due to the progress of hydration of the various components of the used mixtures. The main hydration products for all mixes are calcium silicate hydrate (CSH) and calcium hydroxide (CH) in addition to the hydrates of the aluminate phases. In the mixes which contain GBFS or MK, the liberated calcium hydroxide from the hydration of silicate phases (C3S, β-C2S) of Portland Cement are supposed to react with the silica in both minerals produces more (CSH) which is considered the main bending agent. The formed calcium silicate hydrates have the following formula; CaOx.SiO2.H2Oy (CxSHy), where x and y may vary over a wide range. This depends on many factors such as; water/solid ratio, composition impurities, temperature and time of hydration. Pervious study [9] showed that the initially formed high lime CSH (having high water content) transforms into low lime and low water content- CSH.

The mixes with cobalt chloride showed higher water content than those without cobalt chloride at most of the hydration ages. As the concentration of cobalt ions increases from 2 to 3% by weight of the solid, the combined water increases accordingly.
1. 2. Compressive Strength

A decrease in the compressive strength values can be observed on the addition of Co ions compared with those of the control mixes (Fig. 2). Increasing the ratio of Co$^{2+}$ ions from 2.0% to 3.0% showed larger decrease in the compressive strength values. The decrease of compressive strength may be due to the formation of Co(OH)$_2$ which can form a complex with Ca(OH)$_2$ that gives low strength. As previously discussed all soluble chlorides or halides act as accelerators and not retarders $^{[9]}$.

3. 1. 3. Phase composition

The well crystallized hydration product of ordinary Portland Cement or that blended with GBFS or MK is the calcium hydroxide (CH) phase. Therefore, the change in the intensity of the characteristic peaks of CH can be considered as an indication for the degree of

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Fig. 1. Combined water content versus hydration age of the various mixes.
hydration of the investigated cement pastes. It is obvious from Table 2 that the intensity of CH peaks increases with increasing hydration time for all mixes. This may be due to the progress of the hydration reaction with time. Mixes (MIII) and (MV) which contain GBFS and MK respectively, show less CH compared to the neat cement mix (MI). This can be attributed to the pozzolanic reaction of GBFS and MK with the liberated (CH) as a result of Portland Cement hydration. All mixes with 3.0% Cobalt ions show less intensity for CH peaks compared with the mixes without cobalt. This could be an indication for the retarding effect of cobalt chloride for the hydration of the investigated mixes. Such result is correlated with the obtained results of the compressive strength determination in Table 2.

**TABLE 2. X-ray diffraction analysis of mixes (I, III and V) in presence and absence of Co ions at various ages.**

<table>
<thead>
<tr>
<th>Times (day)</th>
<th>MI</th>
<th>MIC₂</th>
<th>MIII</th>
<th>MIIC₂</th>
<th>MV</th>
<th>MVC₂</th>
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<tr>
<td>1</td>
<td>CH(ms)</td>
<td>CH(m)</td>
<td>CH(m)</td>
<td>CH(w)</td>
<td>CH(m)</td>
<td>CH(ms)</td>
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<tr>
<td></td>
<td>CSH(w)</td>
<td>CSH(vw)</td>
<td>CSH(vw)</td>
<td>CSH(vw)</td>
<td>CSH(w)</td>
<td>CSH(w)</td>
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<tr>
<td></td>
<td>C₃S&amp;β-C₂S</td>
<td>C₃S&amp;β-C₂S</td>
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<td>3</td>
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<tr>
<td>7</td>
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<td>90</td>
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<td>CH(vs)</td>
<td>CH(ms)</td>
<td>CH(s)</td>
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<td>(w)</td>
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<td>(w)</td>
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</tbody>
</table>

Where; CSH: Calcium silicate hydrate, CH: Calcium hydroxide, C₃S: Tricalcium silicate (Alite), β-C₂S: dicalcium silicate (belite).

vw: very weak, w: weak, m: medium, ms: medium strong, s: strong, vs: very strong, and vvs: very very strong
Fig. 2 Compressive strength versus hydration age of various mixes.

Hydration Time (days) [log scale]
3.2 Leaching behavior

3.2.1 pH measurements

The measured pH values of the leachate solution for most mixes were in the range 11.42-13.50 during the hydration period (1-90 days).

3.2.2 Degree of immobilization

Tables 3 and 4 show the values of the degree of immobilization of the different hardened cement pastes containing 2.0 and 3.0% Co ions by weight of solid respectively using the static leaching process. Generally, all pastes show a slight and continuous decrease in the immobilization percent with increasing leaching period up to 90 days. The highest immobilization degrees after 90 days were 99.992 % of mixes containing 40% Slag MIIC2, Whereas, the least immobilization percent were 99.979 % of the mixture containing 20% Slag MIIC1 (Table 3,4). This high degree of immobilization of Co$^{2+}$ ions can be attributed to the competition between the following processes; The precipitation of Co$^{2+}$ ions as Co(OH)$_2$ with Ksp of $5.92 \times 10^{-15}$; oxidation of some Co II to Co III during the hydration process of Portland Cement due to the low oxidation potential of Co at the high pH values of the different binders (pH>12.5) $^{[2]}$ and precipitation of Co(OH)$_3$ of Ksp = $1.6 \times 10^{-44}$.


b. The relatively low sorption capacity of cobalt ions on the formed C-S-H $^{[11]}$. 

TABLE 3. The immobilization % of Co ions of various mixes with 2.0% CoCl₂ (static mode) at various leaching times

<table>
<thead>
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<th>Mixes</th>
<th>Immobilization %</th>
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</thead>
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<td></td>
<td>1</td>
</tr>
<tr>
<td>MIIVC₁</td>
<td>99.996</td>
</tr>
<tr>
<td>MIIC₂</td>
<td>99.997</td>
</tr>
<tr>
<td>MIC₂</td>
<td>99.996</td>
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</tbody>
</table>

TABLE 4. The immobilization % of Co ions of various mixes with 3.0% CoCl₂ (static mode) at various leaching times

<table>
<thead>
<tr>
<th>Mixes</th>
<th>Immobilization %</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>1</td>
</tr>
<tr>
<td>MIIC₂</td>
<td>99.997</td>
</tr>
</tbody>
</table>

4. Conclusions

- Blended Portland Cement pastes with slag or metakaolin showed less values of compressive strength compared to neat Portland Cement paste at all hydration ages up to 90 days.

- The retardation of the hydration caused by CoCl₂ Chloride in all the examined pastes is more likely to be due to formation of a gelatinous surface layer as well as formation of plumbate ions. These reactions consume calcium and hydroxide ions from solution and delay
the supersaturation and precipitation of calcium hydroxide and development of CSH gel.

- XRD analysis did not indicate the formation of any new phases, but did confirm the retarding effect caused by cobalt chloride.
- All pastes showed high degree of immobilization of cobalt but Portland Cement – 40% Slag blended showed the highest values.

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قسم الكيمياء-كلية البنات-جامعة عين شمس-القاهرة
قسم الكيمياء-كلية البنات-جامعة عين شمس-القاهرة.

علم المواد- البناء والإسكان الوطني، مركز البحوث- القاهرة، مصر.

المستخلص: نظراً للتطور الصناعي الهائل في شتى المجالات، أزدادت المخلفات الصناعية المحتوية على الكوبالت. تمثل هذه المخلفات مشكلة بيئية خطيرة لما لها من آثار ضارة جدًا بالبيئة. لذلك أهتم العلماء بدراسة كيفية التخلص الأمثل لهذه المخلفات وذلك باستخدام طريقة التثبيت لهذا العنصر في منتج نهائي صلب لتقليل درجة تسربه إلى البيئة. تم استخدام عدة مخلوطات من الأسمنت هي: أسمنت بورتلاند، أسمنت بورتلاند مخلوط بنسبة 20، 40% من خبث أفران الحديد الأوكاولين المحروق وملح كلوريد الكوبالت في هذه الدراسة. استخدم نسبتين من هذا العنصر هي 2 و3% في صورة ايون ثم أضفت هذه النسبة في ماء الخلط.
أتم تحضير عدة مخاليط أسمنتية باستخدام نسبة ماء في وجود
وعدم وجود الكوبالت وتم إجراء الاختبارات التالية:

1- تعليق محتوى الماء المتحد كيميائيا وقوة التحمل الميكانيكي
لمخاليط المختلفة في وجود وعدم وجود هذا العنصر عند أزمنة
التآرد ت 7.1، 28، 90 يوم.

3- تحليل حيوى أشعة- X لمعرفة التركيب الصنف لتوت
التآرد.

4- قياسات التسرب لهذه الأجسام وتشمل:

أ- قياس pH لمحلول التسرب.

ب- قياس كمية الأجسام المنسرة (مليجرام/لتر) وبالتالي
معرفة درجة الثبات عند أزمنة مختلفة حتى 90 يوم.

ويمكن تحديد أهم ما حصل عليه من نتائج فيما يلي:

1- أوضحت نتائج التحمل للضغط الميكانيكي وتحليل حيوى
أشعة- X (XRD) أن ملح الكوبالت المستخدم في هذه الدراسة له
تأثير مثبط لعملية التآرد للمخاليط الأسمنتية المختلفة خاصة في
الأزمنة المبكرة.

2- أوضحت نتائج قياس محتوى الماء المتحد كيميائيا أن نواتج
التآرد وخاصة كتلات الكادميوم المتأخرة (CSH) لها محتوى
ماء عالي في الخلايا المحتوية على عنصر الكوبالت مقارنة
بالخلطات غير المحتوية على هذا العنصر.

3- بشكل عام كل خلايا المختبرة المستخدمة أعطت درجة
 عالية من التثبيت في وجود الكوبالت مع بعض التفاوت في درجة
التثبيت بأختلاف الخلايا الأسمنتية.

4- تعتبر خلايا الأسمنت البرتغالى الخالص أفضل الخلطات
لتثبيت عنصر الكوبالت. حيث وصلت درجة التثبيت بعد 90 يوم
من الغمر في الماء إلى 1% من القيمة الأصلية المضافة إلى الخلطة.