1999


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CHARACTERIZATION OF SOLIDIFICATION / STABILIZATION OF CHROMIUM
WASTES IN CEMENT MATRIX

A Dissertation

Submitted to the Graduate Faculty of
Louisiana State University and
Agriculture and Mechanical College
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy

In

The Department of Chemistry

by

Aijun Zhang
M.S., Beijing Normal University, Beijing, China. 1985
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ABSTRACT

A cement-based solidification/stabilization (S/S) system of Cr wastes treatment has been studied in this program. A combination of the two techniques; namely reduction of Cr(VI) to Cr(III) and simultaneous immobilization within a cement matrix, has been found to be effective and practical to treat Cr wastes.

Cr(VI) can not be easily and effectively immobilized in the S/S system unless being reduced to Cr(III). Ferrous compounds are used as reducing reagents. The reduction not only removes the toxic Cr(VI) species but also results in the low-solubility precipitation of \((\text{Cr}_x\text{Fe}_{1-x})\,(\text{OH})_3(\text{S})\) in the S/S system. Long-term and short-term samples were tested through TCLP procedure. For appropriate contents and time, the leachate concentrations can be brought below the EPA characteristic limit of 5 mg/L. Usually, the long-term samples show higher leaching concentration of Cr.

Many metal ions have a profound influence on the cementitious matrix formed during the curing process of Portland cement. There is a consensus view, based on calorimetric studies, that Cr species are accelerators for early hydration of cement. This program has been investigating the system in most detail with \(^{29}\text{Si}\) MAS NMR, which shows retarded hydration by Cr salts alone, or by ferrous chloride (or sulfate) alone or in combination with Cr species. In addition to retarded hydration, the added Cr species and ferrous salts results in enhanced amounts of chain-lengthening and chain-branching silicates.

X-ray absorption fine structure (XAS) was successfully applied in speciation of Cr(III) and Cr(VI) in this program. The ratio of Cr(VI) to total Cr in a cement-based S/S
system was measured, and the effectiveness of different Fe(II) reductants is determined from XANES and compared to leachability results. EXAFS analyses revealed a complex situation in the structural picture of the product (or products) of the Cr wastes treatment system in the OPC cement matrix.
CHAPTER 1
INTRODUCTION

Chromium is one of the heavy metals introduced into the environment from widespread use in industrial applications such as electroplating, painting, tanning, metallurgy and textiles\textsuperscript{[1][5]}. The most common oxidation states of Cr in natural waters are Cr(III) and Cr(VI), and they are interconvertible under natural conditions \textsuperscript{[14]}. Toxicity studies show that there is a vast difference between Cr(III) and Cr(VI) ions. While Cr(III) is less toxic, 2 mg/kg Cr(VI) can produce cellular and skeletal damage\textsuperscript{[6]} and there have been many studies linking exposure to Cr(VI) compounds with respiratory cancer, lung cancer and skin damage\textsuperscript{[7][8]}.

The existing treatment processes for Cr involve the reduction of Cr(VI) to Cr(III), which may be followed by solidification/stabilization (S/S) technology. Fe(II) compounds are the most commonly used reducing reagents reported in the literature. The reduction of aqueous Cr(VI) by aqueous Fe(II) not only removes the toxic Cr(VI) species from solution but also results in the precipitation of \((\text{Cr}_x\text{Fe}_{1-x})\text{(OH)}_3\). The solubility of this solid limits Cr(III) concentrations, over the pH range of approximately 5.0-11.0, to less than that of the drinking water standard \textsuperscript{[2]}.

S/S is an economical process for the disposal of many types of hazardous wastes. The method involves mixing liquid or semisolid wastes with binders to produce a solid that is structurally sound and relatively impermeable. Binders often consist of Type I Portland cement (ordinary Portland cement, OPC) or OPC plus fly ash, kiln dust and other pozzolanic materials. It appears that cementitious S/S can involve either
chemical transformations of wastes or microscopic encapsulation, or both. In particular, the use of a cement matrix for the immobilization of inorganic compounds has been considered to be practical because of the special properties of cement, including high pH(12.5) generated during the hydration of calcium silicate \( [5][3][4] \). On the other hand, the amount of chemical compounds, those added as wastes and those formed during the cement hydration and other reactions, will affect the cohesion and strengthening properties of calcium silicate hydrate \( (3\text{CaO} \cdot 2\text{SiO}_2 \cdot 3\text{H}_2\text{O}) \), which is primarily responsible for the resulting mechanical strength of cement samples after set \([3]\).

Combination of the two techniques outlined above, namely reduction of Cr(VI) to Cr(III) and simultaneous immobilization within a cement matrix, is the subject of the current research. This work confirms the utility of this approach through leaching studies. Cr(III) was effectively immobilized by Type 1 Portland cement (ordinary Portland cement, OPC) matrices, as judged by TCLP (toxicity characteristic leaching procedure) \([125]\) leachability. Cr(VI), on the other hand, was poorly immobilized by a wide variety of cement-based binders. Furthermore, the profound effects on the OPC matrices of the retained Cr ions and added ferrous sulfate, ferrous chloride and iron oxide \( (\text{Fe}_3\text{O}_4) \) have been investigated in detail. \(^{29}\)Si MAS NMR revealed retarded hydration by Cr salts alone, or by ferrous compounds alone or in combination with Cr salts. Again, there were major differences between Cr(III) and Cr(VI) in matrix effects. Cr(III) had dramatic long-term effects on OPC matrices, retarding silicate hydration and polymerization.

The differences between Cr(III) and Cr(VI) are not surprising, because the chemistry for Cr(III) and Cr(VI) is quite different. However, the nature of the chemical
interaction between waste metal ions and fixing agents is not well understood. Even basic information on the speciation of Cr ions in such a complex solid system is difficult to obtain by traditional chemical methods.

The phenomenon of X-ray absorption fine structure (XAFS) is commonly referred to as the combination of XANES (X-ray absorption near-edge structure) and EXAFS (extended X-ray absorption Fine structure). XAFS, with the advent of intense synchrotron radiation, is a powerful, nondestructive, element-specific spectroscopic technique applicable to almost all elements of the periodic table in most types of phases. For the speciation study of Cr, XANES has been employed to directly observe the ratio of Cr(VI) to total Cr in a cement-based S/S system by measuring the characteristic pre-edge 3d-4p mixing absorption peak that is proportional to the amount of Cr(VI) in a chromium-containing sample. EXAFS is also successfully applied to obtain valuable information about structure and local environment of Cr species in the complex OPC matrix.
2.1 In the Environment

Background ambient air concentrations of Cr range from as low as 0.005 nanograms per cubic meter (at the South Pole) to as high as 0.684 micrograms per cubic meter (industrial United States) with the average across the US of 0.005 to 0.157 micrograms per cubic meter. Because of its stability, this chromium is assumed to be trivalent.\[6\]

The chromium concentration in US waters varies with the type of industrial sources and soils surrounding the water. Studies done by Cary \[1\] of 170 lakes in the Sierra Mountains found only two of them to contain as much as 5ppb. EPA studies in 1974-75 showed extremes of 0.4 to 8 ppb in 4,000 drinking water sources sampled in the US. Average ranges of chromium in domestic soil are 14 to 70 ppm.\[6\]

An EPA report prepared by the Radian Corp \[10\] estimated that 5,000 metric tons of chromium from industrial and inadvertent sources were admitted into the environment each year. Table I shows Radian's estimate of these sources.

The present limit for dissolved Cr in drinking water is 0.05 mg/L \[13\]. 5 mg/L is the level that requires that industrial wastes be treated to lower Cr concentrations before discharge to the environment. \[7\]

2.2 Toxicity

Acute toxicity studies show that there is a vast difference between tri- and hexavalent chromium ions. Oral LD\(_{50}\) (dose lethal to 50% of recipients) for trivalent salts
Table 2-1. Estimates of Atmospheric Cr Emissions

<table>
<thead>
<tr>
<th>Source Category</th>
<th>Metric Tons per year</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr oil refining</td>
<td>3</td>
</tr>
<tr>
<td>Cr chemical production</td>
<td>450-900</td>
</tr>
<tr>
<td>Ferro-Cr production</td>
<td>43</td>
</tr>
<tr>
<td>Refractory production</td>
<td>90</td>
</tr>
<tr>
<td>Sewage sludge incineration</td>
<td>25-30</td>
</tr>
<tr>
<td>Steel production</td>
<td>2870</td>
</tr>
<tr>
<td>Utility cooling towers</td>
<td>5</td>
</tr>
<tr>
<td>Cement production</td>
<td>16</td>
</tr>
<tr>
<td>Combustion coal-oil(gas) boilers</td>
<td>737</td>
</tr>
<tr>
<td>Process heaters</td>
<td>556</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td><strong>4825 - 5275</strong></td>
</tr>
</tbody>
</table>

Ref. [10]
varies from 135 mg/kg to greater than 10,000 mg/kg. For hexavalent chromium 2 mg/kg can produce cellular and skeletal damage\textsuperscript{[6]}.

It has been well known that many chromium compounds can damage the skin. Allergic contact may arise from either tri- or hexavalent compounds, but the hexavalent ion is responsible for most reported problems. The hexavalent ion penetrates undamaged skin and is subsequently reduced to trivalent, which combines with protein\textsuperscript{[7][8]}.

There have been many epidemiological studies linking exposure to chromium compounds with respiratory cancer. Whether these studies implicate hexavalent chromium alone or trivalent as well is not well known. Most of these studies have been done with the chromate pigment industry. While it was shown that some pigments such as calcium chromate consistently produced lung tumors in rats, it was also shown that all of the pigments produced some lung tumors\textsuperscript{[7][8]}.

Trivalent compounds administered by any means have not been reported as a problem. Animal biopsy studies suggest that hexavalent chromium compounds (particularly soluble and slightly soluble compounds) are probably the agents which are responsible for human related cancer. Under the rules of the International Agency for Research on Cancer (IARC)\textsuperscript{[9]}, the animal assay tests and related human data place hexavalent chromium compounds in group I, meaning there is decisive evidence for the human carcinogenicity of these compounds.

2.3 Treatment of Chromium Wastes

The existing chemical treatment processes involve the reduction of Cr(VI) to Cr(III). Fe(II) compounds are the most commonly used reducing reagents reported in literature, and the capacity of Fe(II) to reduce Cr(VI) is well demonstrated\textsuperscript{[2]}. 

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Conventional reduction of Cr(VI) is performed under acidic conditions (pH value is about 3) utilizing either a ferrous salt or a reduced sulfur compound. The pH is then raised to 8 - 10 for hydroxide precipitation.

\[ 3\text{Fe}^{2+} + \text{HCrO}_4^- + 7\text{H}^+ \rightarrow 3\text{Fe}^{3+} + \text{Cr}^{3+} + 4\text{H}_2\text{O} \]

Espenson quantified the rate of the reaction as:

\[
\frac{d[\text{HCrO}_4^-]}{dt} = -\frac{[\text{Fe}^{2+}][\text{H}^+]^3(\text{k}_1[\text{HCrO}_4^-]+\text{k}_2[\text{HCrO}_4^-]^2)}{[\text{Fe}^{3+}]} \]

The work has been the basis for claims that Cr reduction is very slow at all but acidic pH levels. Each unit increase in pH would decrease the rate of the reaction by 3 orders of magnitude.

Completely contrary to the Espenson rate equation, Higgins and other researchers indicated that Cr\(^{6+}\) could be rapidly and stoichiometrically reduced by ferrous sulfate at pH 7-10. Higgins clarified this apparent discrepancy. Espenson's work was done with very large (and, hence, assumed constant concentrations of Fe(III)) at a very acidic pH. However, at near neutral or alkaline pH levels, the solubility of the Fe(III) depends on the concentration of hydroxide (OH\(^-\)) as follows:

\[
\text{Fe}^{3+} + 3\text{OH}^- \rightarrow \text{Fe(OH)}_3
\]

Using: \(K_{sp}=[\text{Fe}^{3+}][\text{OH}^-]^3\) and \(K_w=[\text{H}^+][\text{OH}^-]\).
combining and substituting into Espenson's equation, the result is an expression independent of pH:

\[
\frac{d[HCrO_4^-]}{dt} = -\frac{[Fe^{2+}]^2k_w^2(k_1[HCrO_4^-] + k_2[HCrO_4^-]^2)}{K_{sp}}
\]

Higgin's work has opened the full pH range for chromium reduction.

Eary\textsuperscript{[2]} also indicated that the most efficient method for removing aqueous Cr(VI) is by the simple addition of Fe(II) salts. Aqueous Fe(II) quantitatively reduces aqueous Cr(VI) over the pH range of 2.0 - 10.0 even in oxygenated solutions. The reaction is rapid with complete reduction occurring within 5 min. However, at higher pH, the competitive oxidation of aqueous Fe(II) by dissolved oxygen produces nonstoichiometric reduction of aqueous Cr(VI). The precipitate was suspected to form from the reaction:

\[
xCr(III) + (1-x)Fe(III) + 3H_2O \rightarrow (Cr_xFe_{1-x})(OH)_3 (s) + 3H^+
\]

where \(x\) can vary from 0 to 1.

In order to determine the extent of Cr(VI) reduction by Fe(II) in oxygenated environments, Fendorf and Li\textsuperscript{[29]} compared the rate expression for the oxidation of Fe(II) by O\textsubscript{2}(g):

\[
-\frac{d[Fe(II)]}{dt} = k_{fe}[Fe(II)] [OH^-]^2 pO_2
\]
with the rate expression for the oxidation of Fe(II) by Cr(VI):

$$-\frac{d[Cr(VI)]}{dt} = k_{cr}[Fe(II)]^{0.6}[Cr(VI)]^1$$

and found that even at low concentrations of 10 \( \mu M \), Cr(VI) will oxidize Fe(II) more rapidly than oxygen at pH values less than 8.0. Oxygen would limit Cr(VI) reduction only at very high pH values (pH > 8) or very low Cr(VI) concentrations (Cr(VI) \(< 10 \mu M \)). As a consequence, Fe(II) should be an effective reductant of Cr(VI) under most soil and water conditions.

Fe(II) was recognized as the dominant reductant of Cr(VI) in a forested wetland soil system at redox level less than +100 mV \[^{30}\]. The role of Fe(II) is especially important when biological activity is limited. It was observed that under mildly reducing conditions Fe(II) species were the major reductant of Cr(VI) in sands and gravels of a suboxic aquifer \[^{31}\]. Even well-crystallized iron oxides such as goethite (\( \alpha \)-FeOOH) can have small amounts of Fe(II) that lead to the reduction of Cr(VI) \[^{32}\].

The reduction of Cr(VI) to Cr(III) by Fe(II) is one of the major methods. A number of other approaches to the treatment of Cr(VI) wastes have been proposed. These methods can be divided into two types: reduction processes with reducing agents other than iron, and direct fixation processes using ion exchange, absorption or precipitation technologies \[^{33-49}\].
2.4 Chromium Chemistry

2.4.1. Hydrolytic Species

The hydrolysis of chromic ion [Cr(III)] produces the mononuclear species CrOH\(^{+2}\), Cr(OH)\(^{2+}\), Cr(OH)\(^{4+}\) and the neutral species Cr(OH)\(^{0}\). The polynuclear species Cr\(_2\)(OH)\(^{2+}\) and Cr\(_3\)(OH)\(^{4+}\) form slowly at 25°C \(^{[14]}\).

The hydrolysis behavior of Cr(III) is complicated by its polymerization reactions. As early as 1908, Bjerrum postulated the presence of a dimeric species from pH titration experiments \(^{[15]}\). Subsequent to Bjerrum’s work, the dimer has been studied extensively in solution \(^{[16]-[19]}\) and its configuration, (H\(_2\)O)\(_4\)Cr(OH)\(_2\)Cr(OH)\(_2\)\(^{2+}\), has been established. Higher degree polymers were also reported by many researchers including Thompson \(^{[19]}\) and Stunzi, et al. \(^{[20]}\).

Because Cr(VI) hydrolyzes extensively, only neutral or anionic (hydroxo or oxo) species occur in water. All stable Cr(VI) complexes are anionic oxyspecies. The anionic form varies according to pH and may be in the forms of chromate (CrO\(_4\)\(^{-2}\)), hydrochromate (HCrO\(_4\)), or dichromate (Cr\(_2\)O\(_7\)\(^{-2}\)). At low pH and high total chromium(VI) concentration, the dichromate ion predominates. Dichromate would become important only at very high Cr concentrations (>10\(^{-2}\) M), which might occur in cases of heavy industrial pollution. At pH > 6.5, Cr(VI) is in the form of the chromate ion. The predominant Cr(VI) species that might exist in natural water are hydrochromate and chromate \(^{[14]}\).

2.4.2. Redox Reactions

The two important oxidation states of Cr in natural waters are III and VI. Laboratory studies have indicated that Cr(III) and Cr(VI) are interconvertible under
natural conditions. Cr(III) is oxidized in natural waters by a large excess of MnO₂; oxidation by oxygen occurs slowly under natural water conditions. Ultraviolet light may promote oxidation of Cr(III) to Cr(VI). Complexed Cr(III) can have different redox behavior from that of the aquochromium (III) ion[14].

Cr(VI) is a strong oxidizing agent in acidic waters but is relatively stable in most natural waters. Species such as CrO₃₂⁻, CrO₄⁻² and CrO₂Cl⁻ strongly oxidize organic matter on contact. In natural waters containing organic matter, Cr(VI) can be reduced to Cr(III), which is then precipitated as Cr(OH)₃. Cr(VI) is also easily reduced by Fe⁺², H₂S, dissolved sulfides, cysteine and mercaptosuccinic acid[14].

Organic reductants of Cr(VI), e.g. soluble organic acids (citric acid, DTPA, fulvic acids and water-soluble organic matter from air-dried soil), may form soluble chelated complexes with Cr(III) in solution above the pH at which uncomplexed Cr precipitates, thus enhancing the mobility of Cr and the potential for re-oxidation to Cr(VI) [21-22]. For example, Cr(III) in citric acid remained soluble up to pH 7.0 - 7.5, whereas Cr(III) in water (no organic ligand added) was precipitated between pH 4.5 - 5.5. Thus, above pH 4.7, Cr could be complexed as Cr(OH)²⁺, or as an polymer. A possible structure is given in Fig. 2-1.

Added Cr-citrate remained soluble for at least one year in a limed soil sample [21]. The oxidation of Cr(III) in tannery sewage sludge and in tannery effluent added to Typic Eutrochrept soil was studied [22]: adding citric acid to the soil along with the tannery wastes increased the amount of Cr(VI); mutual facilitation of Cr(III) oxidation by chelation and of further chelation by oxidation was postulated as a possible mechanism for the continuous formation of Cr(VI) in the soil.
Fig. 2-1. Schematic representation of a possible form of Cr-citrate in an aqueous system with a pH greater than the pKa of the uncomplexed COOH group [22].
Inorganic reductants, e.g., Fe(II), eliminate the possibility above by promoting the formation of Cr(III) solids of very low solubility \[^{[23]}\]. Moreover, the formation of a solid Cr(III) phase will greatly diminish the potential for transformation back to Cr(VI) \[^{[24]}\].

2.4.3. Solubility/Precipitation

The concentration of chromium in natural waters is limited by the low solubility of Cr(III) species. The solid phases that are most likely to control Cr concentrations in surface environments are Cr(III) oxides, Cr(OH)_3 and Cr(III) coprecipitated with Fe oxides. The precipitation/dissolution kinetics of Cr(OH)_3 are rapid, and the solubility between pH 6 and pH 10.5 is very low \[^{[25]}\]. The solubility product for the hydroxide at pH 8.5 is 2.9 x 10^{-29} \[^{[14]}\].

Among all the Cr(III) solid phases for which data are available, the coprecipitate of Cr\(_x\)Fe\(_{1-x}\)(OH)_3 is the least soluble \[^{[23]}\]. Cr(III) and Fe(III) have like charge and similar ionic radii (0.63 \(\Omega\) and 0.64 \(\Omega\) respectively \[^{[26]}\]). Amorphous hydroxide precipitates of these elements, Cr\(_x\)Fe\(_{1-x}\)(OH)_3 form readily at room temperature and behave thermodynamically like true solid solutions. Aqueous Cr in equilibrium with Cr\(_x\)Fe\(_{1-x}\)(OH)_3 at the low Cr mole fractions expected in geologic environments, is several orders of magnitude lower in concentration than when in equilibrium with Cr(OH)_3 \[^{[23]}\].

Cr (III) solubility varies with water characteristics such as hardness, alkalinity and salinity. Cr(III) has low solubility in seawater. The low solubility of Cr(III) solids under neutral or basic conditions limits its rate of reaction (e.g., with oxygen); thus, precipitated Cr(III) can persist under conditions in which it is thermodynamically unstable \[^{[14]}\].
BaCrO₄, PbCrO₄, and Ag₂CrO₄ readily precipitate from solution. Log $K_s$ values at zero ionic strength and 25°C are -9.67 [Ba(II)], -13.75 [Pb(II)], and -11.92 [Ag(I)]\textsuperscript{[14]}.
Cement is a fine-powdered, calcareous material that when mixed with water forms a plastic paste that hardens to a stone-like material. Cement is a very complex material whose hydration involves complicated chemical reactions. Those chemical reactions become even more complex when cement admixtures are used.

The specifications with which cements in different countries must comply are similar, but not identical. Various names are used to define the same type of cement material, such as OPC (Ordinary Portland Cement) in the UK, or Type I Portland Cement in the USA. It is by far the most common cement used in the United States. It is the type of cement used in this research and will generally be referred to as OPC.

3.1 Composition of Cement

Portland cement is made by heating a mixture of limestone and clay (or some other source of silica) at 1400 to 1600 °C, forming a mass called clinker. A small amount of gypsum is added and the clinker is ground to a fine powder.

A typical oxide composition of the cement clinker is presented in Table 3-1. The major phases present are given in Table 3-2.

Alite (C₃S) reacts quickly with water, and is the most important phase in normal Portland cement for strength development, especially at ages up to 28 days.

Belite (C₂S) reacts slowly with water, thus contributing little to the strength during the first 28 days, but substantially to the further increase in strength that occurs at later ages. By one year, the strength contributions from alite and belite are about equal.
<table>
<thead>
<tr>
<th>Oxide</th>
<th>Weight Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaO</td>
<td>67%</td>
</tr>
<tr>
<td>SiO₂</td>
<td>22%</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>5%</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>3%</td>
</tr>
<tr>
<td>Other oxides</td>
<td>3%</td>
</tr>
</tbody>
</table>

Ref. [50]

<table>
<thead>
<tr>
<th>Phase</th>
<th>Chemical</th>
<th>Notation</th>
<th>Weight Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alite</td>
<td>Tricalcium Silicate</td>
<td>C₃S</td>
<td>50-70%</td>
</tr>
<tr>
<td>Belite</td>
<td>Dicalcium Silicate</td>
<td>C₂S</td>
<td>15-30%</td>
</tr>
<tr>
<td>Aluminate</td>
<td>Tricalcium Aluminate</td>
<td>C₃A</td>
<td>5-10%</td>
</tr>
<tr>
<td>Ferrite</td>
<td>Tetracalcium Alumino ferrite</td>
<td>C₄AF</td>
<td>5-15%</td>
</tr>
</tbody>
</table>

Ref. [50]

Cement Chemical Nomenclature:

C = CaO, S = SiO₂, A = Al₂O₃, F = Fe₂O₃,
S = SO₃, H = H₂O

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The aluminate (C$_3$A) phase reacts rapidly with water, and can cause undesirable rapid setting unless a set-controlling agent, like gypsum, is added.

The rate at which the ferrite phase (C$_4$AF) reacts with water appears to be somewhat variable, but in general is slower than that of C$_3$A$^{[50]}$.

### 3.2 Hydration of Cement and the Osmotic Model

Hydration of OPC is a sequence of overlapping chemical reactions leading to continuous cement paste stiffening and hardening$^{[51]}$. Hydration is the totality of the changes that occur when an anhydrous cement or one of its constituent phases is mixed with water. The reactions are more complex than simple conversions of anhydrous cement into a hydrate$^{[50]}$.

When water is added to cement, the alkali sulfates (e.g. gypsum) and aluminates (C$_3$A and C$_4$AF) are rapidly dissolved. Tricalcium silicate (C$_3$S) begins hydrating and a period of rapid evolution of heat occurs$^{[52]}$. The rate of heat evolution diminishes very quickly, however, and during the so-called “induction period” the Ca$^{+2}$ concentration of the liquid phase reaches supersaturation with respect to Ca(OH)$_2$ (referred to as CH) and consequently, nucleation and growth of both calcium silicate hydrates (C-S-H) and CH begin.

The basic chemical changes of hydration are given in Table 3-3. First, C$_3$A hydrates, causing the rapid setting that produces a rigid structure. Setting rate is controlled by the amount of gypsum added in the cement manufacture. The ettringite that forms does not contribute to setting, but coats the cement particles and retards the setting reactions. Hydration of C$_3$S and C$_2$S, which account for about 75% of the cement
by weight, is responsible for strength development after the initial set. The reaction products in both cases are the same — C-S-H gel and crystalline CH.\textsuperscript{[33]}

Four stages in the hydration of cement are illustrated in Fig. 3-1\textsuperscript{[53]}. Initially, the cement grains dispersed in water appear as in Fig. 3-1(a); after about two minutes calcium sulfoaluminate hydrate (AFt) begins to form on the surfaces of the grains [Fig. 3-1(b)]. Two hours later the sulfoaluminate hydrates, and possibly other hydrates, begin forming an intermeshing network that causes setting [Fig. 3-1(c)]. After two days, the network has developed further due to the hydration of calcium silicates, forming C-S-H gel and causing hardening [Fig. 3-1 (d)].

The major hydration product of OPC is C-S-H gel, which provides the cohesive matrix responsible for strength development of the paste. This gel is amorphous and of variable composition and can adopt a variety of morphologies, which have been variously described as colloidal spheres, crumpled foils, fibers, needles, plates and rosettes\textsuperscript{[50, 54, 55]}.\textsuperscript{[3]

There is a consensus of opinion that gelatinous coatings of C-S-H are formed on the surface of clinker particles soon after contact with water\textsuperscript{[56, 57]}. Such observations provide the basis of protective coating theories of cement hydration. The protective envelope of C-S-H gel formed around the cement grains inhibits further hydration and gives rise to the “dormant” period\textsuperscript{[58]}.\textsuperscript{[3]

The osmotic membrane model of Double \textit{et al}\textsuperscript{[56]} and Birchall \textit{et al}\textsuperscript{[59]} provides one explanation for the end of the dormant period, and subsequent renewed hydration. This model is based on the observation that membranes of C-S-H gel exhibit semi-permeable properties. It is proposed that during the dormant period, water is
Table 3-3 Basic chemical changes

<table>
<thead>
<tr>
<th>Reactants</th>
<th>Products</th>
<th>Heat Evolved (cal/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_3A + 6H$</td>
<td>$C_3AH_6$</td>
<td>207</td>
</tr>
<tr>
<td>$2C_3A + 21H$</td>
<td>$C_4AH_{13} + C_2AH_8$</td>
<td></td>
</tr>
<tr>
<td>$C_3A + 3CS + 32H$</td>
<td>$C_6AS_3H_{32}$ (ettringite)</td>
<td>347</td>
</tr>
<tr>
<td>$2C_2S + 6H$</td>
<td>$C_3S_2H_3$ (C-S-H gel) + 3CH</td>
<td>120</td>
</tr>
<tr>
<td>$2C_2S + 4H$</td>
<td>$C_3S_2H_3$ (C-S-H gel) + CH</td>
<td>62</td>
</tr>
<tr>
<td>$C + H$</td>
<td>CH</td>
<td>279</td>
</tr>
</tbody>
</table>

Ref. [53]
Fig. 3-1 The Phases of Cement Setting.

4-1. (a): cement clinkers

4-1. (b): hydrates begin to form

4-1. (c): hydrates cause setting

4-1. (d): forming C-S-H gel causes hardening.
preferentially pulled through the C-S-H membrane coating and the end of the dormant period occurs when the gel coatings rupture under osmotic pressure. Renewed hydration and growth of secondary hydration products can then take place. The very low solubility of C-S-H gel and the low levels of silica found in solution right from the time of mixing indicate that the hydration reaction cannot occur by a “through solution” mechanism, but must take place on the surface of the cement grains [60, 61, 62].

According to the osmotic model, hydration of cement is controlled by the diffusion of water and solute species through a C-S-H membrane around the cement grains, and so the rate of hydration will depend on the thickness and permeability of these membranes, as well as on the ability of ion species to diffuse through them [56 - 62].

3.3 Effects of Inorganic Admixtures on Hydration of OPC

Industrial wastes containing heavy metals such as Cr, Hg, V, Cd, Pb and Zn, can be disposed of by incorporation into cement matrices, by means of solidification/stabilization (S/S) processes. However, very little is known about the distribution and stability of these contaminants. The use of water-soluble admixtures to accelerate or retard the setting of cement is a well-established practice [63], but not much is known about the effects of the inorganic admixtures in the cement matrix in these cases either.

Salts like calcium sulfate and calcium chloride have been deliberately added to cement. Investigation on the effects of added materials revealed that the setting properties depend on the type and concentration of the salts. With some compounds the set is retarded and with others accelerated. With certain compounds the set is retarded
when they are present in small quantities and accelerated when larger amounts are added [64].

It is proposed that the effect of inorganic admixtures on cement hydration is controlled by their effect on the chemistry of precipitation of the C-S-H gel coatings and the mobility of ions and anions through those coatings. Admixtures that give rise to denser, more compact C-S-H gel coatings will be retarders of the hydration process. Retarders, such as phosphate [63] which have low solubility calcium salts and precipitate as dense coatings incorporated in the C-S-H gel membrane, lead to thickening and loss of permeability of the coating, and hence the process of osmotic pressure build-up, and subsequent rupture of the coating, will be delayed.

The effect of species with soluble calcium salts is twofold. Firstly, they will affect the structure of C-S-H gel coatings through adsorption on to and deflocculation of colloidal C-S-H particles. The more open and permeable the coatings, the greater the acceleration of hydration. Secondly, anion mobility is an important factor. Accelerating anions, such as Cl⁻ and Br⁻, would be expected to diffuse readily through C-S-H coatings to increase internal osmotic pressure and thus facilitate membrane rupture and renewed hydration at the end of the dormant period [63].

3.4 Chromium in the cement matrix

3.4.1. Chromium in the process of cement hydration

Cr(III) and Cr(VI) are the most common oxidation states among Cr compounds in the environment. Cr(VI) is considered to be of major environmental concern. Cr(VI) exist usually as anionic species and Cr(III) as cations. They have significantly different chemistry.
Cr compounds, such as CaCrO₄, CrCl₃, Cr(NO₃)₃ and Cr oxides, have been studied as inorganic admixtures in cement [63, 65, 66, 67, 68, 69]. Differential thermal analysis [63, 66] and compressive strength development [67, 68, 69] showed that Cr accelerated the hydration reaction and strength development in cement.

OPC mixed with various amounts of Cr in the form of nitrates [Cr(NO₃)₃], to simulate industrial waste, was studied by electron microscopy (SEM and TEM/STEM) [65]. The authors proposed that Cr(III) was chemically incorporated in all hydrated cement phases, and appeared to substitute for Si in C-S-H gel and is associated with calcium salts, e.g. Ca(OH)₂ and Ca(NO₃)₂. Cr was also detected in polycrystalline Ca-Cr-rich phases.

SEM analysis indicated the absence of ettringite or any AFt (Al₂O₃·Fe₂O₃·trisulfate) phases in the Cr-containing cement paste. Cr(III) appeared to inhibit the formation of ettringite, which may be related to its role as a hydration accelerator. Gypsum, a known retarding additive, is believed to promote ettringite formation [70]. Ettringite hinders the formation of an aluminasilica gel, which is responsible for the initial rapid set.

SEM and TEM/STEM [65] analysis showed a correlation between the Cr and Si concentrations in the cement paste. As the Cr content increased, the Si content decreased, indicating that Cr might have substituted for Si in the silicate ions, through the formation of CrO₄⁻². There is a charge imbalance, however, as chromium is trivalent and silicon is tetravalent. The researchers [65] suggested that the imbalance might be offset by the presence of other ions like H⁺ or H₂O⁺ associated with each substituted chromium.
Cr(III) substitution into C-S-H has been reported previously by Tashiro \cite{68, 69}. 10% or more of Cr$_2$O$_3$ can enter into solid solution with C-S-H. They suggested that Cr$^{3+}$ substitutes for both Ca$^{2+}$ and Si$^{4+}$.

Among the hydrated cement phases for Cr-containing samples, Ivey et al.\cite{65} observed the monosulfates (AFm) and not the trisulfates (AFt). Significant amounts of chromium were detected in the AFm phases. It is likely that chromium substituted for both Al and Fe, because the ionic charges are the same (3+) and the ionic sizes are comparable.

Ivey et al. consider that retarders tend not to be chemically contained within the cement structure \cite{65}. Pb, for example, is a known hydration retarder and has been found, by photoelectron spectroscopy, to be primarily a surface species in cement paste \cite{71}. This is in contrast to Cr, which was barely detectable at the surface \cite{65}. Retarders form insoluble salts on hydrating phases \cite{63, 71}. This results in a loss of permeability, forming a diffusion barrier to water. The net result is to slow the rate of hydration. Accelerators, such as Cr, have soluble calcium salts and thus are more easily incorporated into the hydration products.

3.4.2). Some Physical properties of Cr-cement samples

Measurements of the physical properties on cement samples containing CrCl$_3$·6H$_2$O, Cr$_2$O$_3$ and CrO$_3$ respectively have been reported by Zamorani et al. \cite{67}. They explained the significant increase in compressive strength of cement samples (Fig. 4.2.) as a result of the formation of Cr(OH)$_3$·nH$_2$O gel \cite{72} which has properties similar to C-S-H gel, and which contributes to the increased mechanical strength of the cement samples.
The formation of Cr(OH)$_3$-nH$_2$O gel may be explained by the following reactions.

In neat cement:

$$2\text{Ca}_3\text{SiO}_5 + 6\text{H}_2\text{O} \rightarrow 3\text{CaO} \cdot 2\text{SiO}_2 \cdot 3\text{H}_2\text{O} + 3\text{Ca(OH)}_2 \quad (3-1)$$

and for cement containing CrCl$_3$-6H$_2$O:

$$3\text{Ca(OH)}_2 + 2\text{CrCl}_3 + n\text{H}_2\text{O} \rightarrow 3\text{Cr(OH)}_3 \cdot n\text{H}_2\text{O} + 3\text{CaCl}_2 \quad (3-2)$$

In neat cement, about 20% of the total pore volume is composed of pores of diameter 350 nm or smaller, whereas, about 55% of the total pore volume in cement containing CrCl$_3$-6H$_2$O is composed of smaller pores of diameter 100 nm or less. The values of compressive strength in cement containing Cr$_2$O$_3$ are lower than those for cement containing CrCl$_3$-6H$_2$O. The authors\textsuperscript{[67]} explained that that might suggest that Cr$_2$O$_3$ could not react with the cement matrix as actively as CrCl$_3$ to produce 3Cr(OH)$_3$-nH$_2$O, which was described in the equation 3-2. The pore size distribution for CrO$_3$ mixed with cement shows that about 60% of the pore volume is made up of pores of diameter 36-55 nm. The effect on pore size distribution is similar to that of Cr$_2$O$_3$.

For Cr(VI) oxide (CrO$_3$) samples, a sharp increase in compressive strength is also indicated by Zamorani et al.\textsuperscript{[67]} for the addition of small amounts of chromium, but addition of larger amounts makes the curve of the strength increase flat.
The increase in compressive strength was explained on the basis of the formation of chromates by the reaction of $\text{CrO}_4^{2-}$, with $\text{Ca}^{2+}$, $\text{K}^+$, and $\text{Na}^+$ ions, resulting in the increased hydration of the cement matrix. This kind of reaction, however, is limited up to a certain concentration of Cr(VI) (i.e., Cr element / cement = 0.015)\textsuperscript{[73]}.

Work in the present thesis will indicate that the explanation is not a reasonable one, since $\text{CrO}_4^{2-}$ does not increase the proportion of hydrated cement.
CHAPTER 4
X-RAY ABSORPTION FINE STRUCTURE

For determining soluble Cr(VI) concentrations, several analytical methods have been recommended by US EPA, including the use of diphenylcarbazide colorimetry, atomic absorption spectrophotometry, coprecipitation, and differential pulse polarography \[^{126,127}\]. For measuring the total concentration of Cr(VI) in solid-water systems, both the soluble and insoluble forms, methods include coprecipitation, acid extractions, iron hydroxide scavengers, and the difference technique with oxidation state conversion \[^{128,129,130}\]. The method considered most effective for measuring total Cr(VI) in soil-water systems is to use a carbonate/hydroxide solution at 90-95 °C to extract Cr(VI) \[^{131}\]. A common and obvious drawback for these methods is that it is almost impossible to confirm that all of the Cr(VI) has been extracted into solution. Other problems include incomplete conversion, solution contamination by the oxidation/reduction reagents, and interference from other metals.

The phenomenon of X-ray absorption fine structure (XAS) is applicable to solve those problems. XAS is commonly referred to as the combination of XANES (X-ray absorption near-edge structure) and EXAFS (extended X-ray absorption Fine structure). XAS is a nondestructive, element-specific spectroscopic technique applicable to almost all elements of the periodic table in most types of phases. Many developments in XAS’s powerful and practical capabilities are tied to the advent of intense synchrotron radiation, which provides a broad spectral range from infrared (\(E \leq 1 \text{ eV}, \lambda > 12,000\AA\)) to hard X-ray (\(E \leq 100 \text{ keV}, \lambda > 0.12\AA\)). The synchrotron radiation is characterized by better signal to noise ratio over a larger energy range, due to the 5 orders of magnitude
increased intensity of synchrotron radiation over that from conventional source \cite{132}.

4.1 XANES (X-ray absorption near-edge structure)

4.1.1. XANES and the K edges of 3d transition metals

XANES is a probe for information about the oxidation state of an absorbing element and the site symmetry and bonding of its local environment.

As a region near an X-ray absorption edge is scanned in energy, the ejected photoelectron sequentially probes the empty electronic levels of the material. The resulting XANES spectrum within about 30 eV of the edge has been realized to be rich in chemical information. But for structure analysis, the data from the near edge region are less utilized because multi-scattering and chemical bonding effects complicate their interpretation \cite{133}.

The 3d metals possess narrow partly filled 3d bands, which give rise to electronic and magnetic properties of physical and technological interest. For example, the 3d band is half full in Cr \((^{24}\text{Cr}\ 3d^54s^1)\). In the 3d transition metals the K edges measured by XAS arise primarily from \(1s \rightarrow 4p\) transitions, although it appears that the initial features observed at the threshold may be due to \(1s \rightarrow 3p\) transitions. When the transition metals are oxidized, they become insulators, and band gaps of a few electron volts open up between the filled valence and unfilled conduction bands. And the edge is shifted upward by a chemical shift, \(\Delta cs\). The interpretation and calculation for compounds is much less clear-cut than for the metals \cite{134}.

The Cr K edge absorption is characterized by pre-edge features, corresponding to the excitation of a core level (e.g. 1s) electron toward bond, or delocalized, empty states. The pre-edge region of the Cr XANES spectra is quite different for Cr(VI) and
Cr(III), because a measurable shift in the X-ray absorption spectrum is correlated to the difference in oxidation states of the element\textsuperscript{[132, 135, 136]}. In a pure atomic frame, the 1s → nd transition is forbidden. However, the effective mixing of the transition metals' d-states with ligand p-states will give a non-zero transition probability. In a molecular orbital bonding scheme, there is strong d-p orbital mixing arising from highly covalent M-O bonds and the lack of a center of symmetry or by a reduction of the inversion symmetry. This was used to explain the high relative intensity of the pre-edge features of Cr(VI)O\textsubscript{4} complex compounds, Fe(III) in a silicate glass of KFeSi\textsubscript{3}O\textsubscript{8}, Ti(IV) in SiO\textsubscript{2} and V(V)O\textsubscript{4} complex compounds\textsuperscript{[132, 137]}. Such a pre-edge resonance is a fingerprint for the presence of species lacking an inversion center and also can provide quantitative information\textsuperscript{[132, 137]}.

In this work we use XANES spectra to directly observe the ratio of Cr(VI) to total Cr in a cement-based S/S system by measuring the characteristic pre-edge 3d-4p mixing absorption peak proportional to the amount of Cr(VI) in a chromium spectrum. The effectiveness of different Fe(II) reductants is determined from XANES and compared to leachability results.

4.1.2). Data analysis

XANES spectra of standard samples containing pure and mixed Cr oxidation states are shown in Fig. 4-1.

The samples containing CrO\textsubscript{4}\textsuperscript{2-} show the distinct absorption peak prior to the main Cr K absorption edge. Spectra were plotted relative to the energy of the pre-edge maximum. All spectra showed additional features near the edge, and the energies and
Fig. 4-1. XANES Spectra of Cr K pre-edge Absorption for Standard Samples

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intensities of these features contain information on the bonding character of the Cr site. However, for transition metals in coordination geometries that lack a center of inversion, the pre-edge peak intensity is more useful for quantitative analysis than energy shifts because the energies of the spectral features superimposed on the edge are more matrix dependent \[^{[138]}\].

In this work, the major pre-edge absorption peak for Cr(VI) was the same for all measurements to within 0.2 eV, which was one monochromator step. The intensity of the peak in the spectra of standards in Figure 4-1 increased with increasing proportion of Cr(VI).

The basic XANES spectral data processing procedure included:

1). Background correction and normalization with WinXAS97 v.1.1 (Thorsten Ressler).

2). Section the normalized spectrum from 5975 eV to 6045 eV, which covers the Cr Kα pre-edge absorption and other pre-edge features.

3). Spline and subtract the baseline of the spectrum in the pre-edge region with PeakFit \^TM 4.0 (SPSS Inc.).

4). Fit the pre-edge peaks and derive the areas of the peaks with the PeakFit software by using the deconvolution function.

The resulting data of peak areas for standard Cr(VI) and Cr(III) samples and associated errors are summarized in Table 4-1. The estimated accuracy of the technique is ±5% in term of Cr(VI)/total Cr \[^{[139]}\].

The normalized areas for the standards exhibit decent linear correlation with the designed proportion of Cr(VI) in the standards (Fig. 4-2).
Table 4-1. Standard Sample Cr K Pre-edge Absorption Peak and corresponding Concentration

<table>
<thead>
<tr>
<th>Cr(VI) (%) of total Cr</th>
<th>Normalized peak area</th>
<th>Peak Fit analysis Standard Error*</th>
</tr>
</thead>
<tbody>
<tr>
<td>0%</td>
<td>0.0077</td>
<td>0.010</td>
</tr>
<tr>
<td>20%</td>
<td>0.0411</td>
<td>0.015</td>
</tr>
<tr>
<td>60%</td>
<td>0.1035</td>
<td>0.010</td>
</tr>
<tr>
<td>80%</td>
<td>0.1489</td>
<td>0.011</td>
</tr>
<tr>
<td>100%</td>
<td>0.2110</td>
<td>0.010</td>
</tr>
</tbody>
</table>

*Standard Error, $S_E = \sqrt{MSE}$.
Mean Square Error, $MSE = \frac{SSE}{DOF}$.

Sum of Squares due to Error, $SSE = \sum_{i=1}^{n} W_i(y_i - \bar{y})^2$.

Degree of Freedom, $DOE = n - m$;
n, the total number of data points; m, the total number of parameters fitted.
Fig. 4-2. XANES of Cr K pre-edge Absorption Standard Curve
4.2. EXAFS (extended X-ray absorption Fine structure).

4.2.1. EXAFS and the X-ray absorption spectrum

EXAFS is a probe of the structural distribution, e.g. interatomic distances, numbers of neighboring atoms (coordination number), and degree of disorder and identity of atoms in the immediate vicinity (about 5 Å) of the absorbing atom [132, 133, 140].

The EXAFS spectrum results from the constructive and destructive interference between the outgoing and incoming photoelectron waves at the central absorbing atom (A) (Figure 4-3). Therefore, EXAFS provides structural information about surrounding atoms (B) in the local three-dimensional environment. It is performed by analyzing the oscillatory fine structure that occurs beyond the edge of the X-ray absorption spectrum of the central atom A.

As seen in Fig. 4-3, the circles associated with each atom pair (A, B) represent wavefronts of outgoing (from A) and backscattered (from B) waves at intervals of the photoelectron wavelength $\lambda$. The interference between the two types of waves is dependent on $\lambda$ (and so the incident X-ray energy) and the nearest atom distance between A and B, $R_{AB}$. The interference results in oscillations in the X-ray absorption spectrum (Fig. 4-4a).

The frequency of EXAFS oscillations is related to the distance between the absorbing atom and the backscattering atoms. The larger the interatomic distances, the shorter periods of EXAFS. The periodicity is also related to the identity of the absorbing and backscattering elements. Each has unique phase shifts. The amplitude of EXAFS is related to the number, type, and arrangement of backscattering atoms around the absorbing atom. The amplitude caused by six neighboring atoms is greater than that
Fig. 4-3. Schematic representation
Of outgoing (from center atom A) and
Backscattering (from surrounding atoms B) wave-process
Fig. 4-4a. Cr K edge absorption spectrum of OPC sample containing Cr(VI) + FeSO₄
Fig. 4-4b. Extracted and weighted EXAFS spectrum of sample containing Cr(VI) + FeSO₄.
Fig. 4-4c. PRDF of OPC sample containing Cr(VI) + FeSO₄
Fig. 4-4d. Curve-fitting of PRDF of OPC sample containing Cr(VI) + FeSO₄
by two of the same atoms at the same distance. The amplitude is also related to the Debye-Waller factor, a measure of the degree of disorder of the backscattering atoms caused by dynamic (thermal-vibrational properties) and static (inequivalence of bond lengths) effects. Finally, there is no EXAFS for an absorbing element with no near neighbors, such as for a noble gas\textsuperscript{[132,133]}.  

4.2.2). Data analysis  

Extraction of structural information from EXAFS is a multi-step procedure.

a). Extraction of $x(E)$ from $\mu(E)$.  

After removal of the underlying background of the spectrum from the overall X-ray absorption oscillations, the first step in the data analysis is extraction of the EXAFS fraction, $x(E)$, of the spectrum. Determination of $x(E)$ requires removal of $\mu_0(E)$ from the X-ray absorption spectrum $\mu(E)$.  

Theoretically, $\mu(E)$ is the measured absorption, and $\mu_0(E)$ is the “smooth” absorption that would be observed at the same wavelength if no EXAFS structure were present (e.g. for an isolated atom). Except in the case of a monatomic gas, it is physically impossible to measured $\mu_0(E)$ experimentally. Therefore, $\mu_0(E)$ must be approximated numerically, which is accomplished by a spline function fitted to the EXAFS portion of the spectrum.

\begin{equation}
\frac{x(E) = (\mu(E) - \mu_0(E))}{\mu_0(E)}
\end{equation}

40

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Equation (4-1) indicates that $x(E)$ is obtained by taking the difference of $\mu(E)$ and $\mu_0(E)$, and normalizing by $\mu_0(E)$ \cite{132, 133, 140}. Both of $\mu(E)$ and $\mu_0(E)$ are contained in Fig. 4-4a.

b). Conversion and weighting of $x(E)$ to $k^2x(k)$.

Fig. 4-4b exhibits the extracted and weighted EXAFS spectrum, $k^2x(k)$, derived from the spectrum in Fig. 4-4a. The energy scale (eV) used in the original absorption spectrum has been converted to the photoelectron wave vector scale or $k$ scale ($\AA^{-1}$), and $x(k)$ has been weighted by $k^2$ to offset the rapid decay of EXAFS oscillations.

$k$ is related to the photoelectron kinetic energy, $E = (E_n-E_0)$, by

$$k = \left[\frac{8\pi^2 m \hbar^2}{\mu(E)} \right]^{1/2}$$

(4-2)

where $m$ is the rest mass of the electron and $\hbar$ is Planck’s constant. For $E$ in eV, $k \equiv 0.51(E)^{1/2}$ ($\AA^{-1}$).

c). Fourier transform of $k^2x(k)$ to PRDF.

$x(k)$ is the sum of individual sinusoidal components arising from the backscattering by different coordination shells. The frequencies of these components primarily depend on the interatomic distance of the coordination shells. Fourier transformation of $k^2x(k)$ produces a frequency spectrum called the Pseudo Radial Distribution (PRDF), as shown in Fig. 4c. The peaks in the PRDF correspond to individual sinusoidal frequencies and, more significantly here, to radial coordination shells. But the radial positions are shifted slightly from the actual nearest neighbor distances, thus they are only approximate or pseudo distances \cite{133, 140}.
d). Structural information and curve fitting.

Besides interatomic distances \(r\), EXAFS contains other structural information such as coordination number \(N\), Debye-Waller factors \(\sigma^2\), the degree of vibrational and static disorder), and the types of neighbor atoms. These structural parameters may be obtained by measuring the EXAFS of model compounds under identical conditions \[^{141}\]. The structure of an unknown is then modeled by curve-fitting procedures so as to calculate EXAFS that best fits the experimental data.

Various curve-fitting methods have been described \[^{133}\]. In this work, FEFF \[^{144}\] program was employed to analyze EXAFS data of samples and to do curve fitting – calculating and simulating structural information of the experimental samples. The variables allowed to "float" during the curve fitting process are \(N\), \(r\), \(\sigma^2\) and \(E_0\). Fig. 4-4d shows curve fitting for the OPC sample containing 4% of Cr(VI) and the stoichiometric amount of FeSO\(_4\) required for reduction. XANES for this sample has shown all Cr(VI) reduced to Cr(III).

Overall, this multi-step data reduction process is a very complex one. Almost every step involves considerable and critical data selections or manipulations, such as pre-edge and post-edge background removal, determination of \(\mu_0(E)\) and then normalization of \(x(E)\), \(k\) weighting, \(k\) space range selection for Fourier transform, module compound selection and theoretical calculations, "floating" of parameters of \(N\), \(r\), \(\sigma^2\) and \(E_0\) during curve fitting, etc.. All these steps raise the uncertainty of the treatment of experimental data. This method is certainly imperfect and far from mature, but its distinct and powerful advantages still make it one of the fastest developing techniques in recent years.
5.1 $^{29}$Si NMR of Solids

Nuclear magnetic resonance spectroscopy is most often used to study the molecular structure of materials in the liquid state. Over the past 20 years, the so-called “magic angle spinning” (MAS) NMR has become routinely available for studying materials in the solid state.

The first solid state NMR studies of the hydration of $C_3S$ were conducted by Lippmaa et al.; they found five ranges of chemical shift from silicates and aluminosilicates, which could be related to the extent of polymerization in the silicate $[74, 75]$. Since then, a significant number of studies on $C_3S$, $C_2S$ and Portland cement has appeared and $^{29}$Si NMR has proved to be a very informative and reliable technique for structural studies in a wide range of silicates and other silicon-containing materials $[76 - 84]$.

$^{29}$Si is a spin $\frac{1}{2}$ nucleus present at about 4.7% natural abundance $[82]$. It gives an NMR signal that is easy to detect with modern instrumentation without artificially enriching the sample. Magic angle spinning (MAS) yields simple spectra with complete averaging of the chemical-shift anisotropy and is, therefore, the most important technique for the measurement of $^{29}$Si NMR of crystalline, amorphous, and glassy solids, which are difficult by other methods. In proton containing samples, line broadening due to dipolar $^{29}$Si-$^1$H interactions can be removed by high power proton decoupling, and cross-polarization (CP) may be used for signal enhancement.
5.2 Interpretation of $^{29}$Si Chemical Shift in Solids

Most of the structural information that can be derived from $^{29}$Si NMR spectra of solids arises from chemical shifts (CS). Since CS is dependent on the electronic environment of the $^{29}$Si nucleus, it should be related to the type, position and bonding characteristics of the surrounding atoms.

The chemical shifts in a $^{29}$Si NMR experiment on silicates or aluminosilicates are mainly determined by the number of Si and (or) Al atoms attached to the specific SiO$_4$ tetrahedra under investigation. In $^{29}$Si NMR the Q$^n$ notation represents the SiO$_4$ tetrahedron, while the superscript $n$ ($n=0, 1, 2, 3$ or $4$) refers to the number of other silicate tetrahedra to which it is linked by sharing O. Q$^0$ is for monosilicates, Q$^1$ disilicates and chain end groups, Q$^2$ middle groups, Q$^3$ chain branching sites and Q$^4$ 3-dimensional cross-linked frameworks. [Table 5-1]

The total range of $^{29}$Si chemical shift in silicates (about 60 to -120 ppm relative to TMS) is related to the degree of polymerization of the SiO$_4$ tetrahedra $^{75}$. It has been shown that hydration of C$_3$S proceeds by formation of dimers and more slowly, linear and cyclic polymers $^{75}$, and silicate dimer is the predominant species in the hydrating cement paste $^{83}$. At later stages, a combination of dimer and/or end units (Q$^1$), and middle units (Q$^2$) is observed, and the latter become increasingly abundant with time of hydration $^{84}$.

There are two characteristic features which affect the $^{29}$Si CS of a SiO$_4$ group: high-field shifts are observed with increasing number of SiO$^T$ bridges ($T=Si, Al$) formed by the SiO$_4$ tetrahedron (degree of SiO$_4$ polymerization), and typical low-field shifts follow from the replacement of Si with Al in the second coordination sphere of
the central silicon with a given number of SiOT bridges (degree of tetrahedral Al substitution). Typical ranges of CS for the central Si atom of the five SiO$_{4-n}$(OSi)$_n$ environments in silicates, the five SiO$_{4-n}$(OAl)$_n$ in framework aluminosilicates and the four Si(OH)(OSi)$_{3-n}$(OAl)$_n$ in layer aluminosilicates have been derived from a lot of experimental data [82]. The CS ranges of the different environments overlap, but it is generally feasible to make the assignment of well separated peaks in the $^{29}$Si MAS NMR spectrum of a certain silicate or aluminosilicate to the corresponding Si environments [82]. Thus, the presence of the degree of polymerization of the constituent silicate groups, the distinct type of structural units and, from peak intensities, their quantitative distribution in the structure can be determined from the $^{29}$Si NMR spectrum.
<table>
<thead>
<tr>
<th>Structure</th>
<th>Notation</th>
<th>Chemical Shift (ppm from TMS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O−Si−O−</td>
<td>Q⁰</td>
<td>-66 to -74</td>
</tr>
<tr>
<td>O−Si−O−</td>
<td>Q¹</td>
<td>-77 to -83</td>
</tr>
<tr>
<td>O−Si−O−</td>
<td>Q²</td>
<td>-86 to -88</td>
</tr>
<tr>
<td>O−Si−O−</td>
<td>Q³</td>
<td>-90 to -100</td>
</tr>
<tr>
<td>O−Si−O−</td>
<td>Q⁴</td>
<td>-100 to -110</td>
</tr>
</tbody>
</table>

Fig. 5-1 $^{29}$Si Chemical Shift Ranges in Solid Silicates
CHAPTER 6
EXPERIMENTAL PROCEDURES

6.1 Preparation of Wastes used for S/S

6.1.1) Materials

Type I Portland cement (OPC) produced by River Cement Company, St. Louis, MO, was used to prepare all samples. The analysis of the cement expressed in terms of oxides, has been provided by River Cement Company, and is shown in Table 6-1.

The following reagent grade chemicals (from Aldrich) were used in preparation of waste samples and standard reference:

\[ \text{Na}_2\text{CrO}_4 \cdot 4\text{H}_2\text{O}, \text{Cr(NO}_3\text{)}_3 \cdot 9\text{H}_2\text{O}, \text{FeSO}_4 \cdot 7\text{H}_2\text{O}, \text{FeCl}_2 \cdot 4\text{H}_2\text{O}, \text{Fe}_3\text{O}_4, \text{Cr}_2\text{O}_3 \]

6.1.2) Sample Preparation

Various cement/waste, cement/additive, and cement/additive/waste recipes were prepared by mixing cement and/or additives with the required amount of waste into 20 mL borosilicate screw cap vials and then adding deionized water. For each study, 10g of cement was mixed with the amount of \( \text{Na}_2\text{CrO}_4 \cdot 4\text{H}_2\text{O} \) corresponding to 1 g, 0.4 g, 0.1 g or 0.01 g of Cr respectively; reducing reagent Fe(II) salt was added with the molar ratio of Fe:Cr of 3:1 or 6:1. The water/cement (w/c) was 0.5 except for the sample containing 1 g Cr and the corresponding Fe(II) salt, which needed 10 mL deionized water for workability. The mixture was stirred vigorously for about 30 - 60 seconds to apparent homogeneity with a thin stainless steel spatula. The samples were allowed to cure in the vials, sealed, and maintained at 23±2°C. Specimens were characterized at cure times from 8 hours to 1 year.
Table 6-1. Chemical Composition of Type I Cement Used in the Present Study

<table>
<thead>
<tr>
<th>Compound</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>20.6%</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>5.2%</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>2.4%</td>
</tr>
<tr>
<td>CaO</td>
<td>64.9%</td>
</tr>
<tr>
<td>MgO</td>
<td>3.3%</td>
</tr>
<tr>
<td>SO₃</td>
<td>2.9%</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.07%</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.56%</td>
</tr>
</tbody>
</table>
6.2. Leaching Analysis

6.2.1. TCLP

The primary objective of S/S treatment is to immobilize (or to change, in some cases) constituents in the waste. Leachability testing is used to predict the degree to which this objective has been accomplished. Because of the variety of possible landfill scenarios, no single leachability testing procedure or protocol can duplicate all possible field circumstances. Therefore, standard leachability tests have been developed and promulgated by the US EPA in the United States.

The environmental acceptability of a hazardous waste for land disposal in the United States is based on the US EPA Extraction Procedure Toxicity (EPT) test or, more recently, the Toxicity Characteristic Leaching Procedure (TCLP) \[^{[33, 125]}\]. The TCLP is designed to determine the mobility of both organic and inorganic contaminants present in liquid, solid, and multiphasic wastes \[^{[121]}\], and to simulate, in at least a gross manner, the leaching potential of a waste under a real-world set of conditions.

An acidic aqueous leaching fluid is used. Two types of extraction fluids are defined in the TCLP, one is an acetic acid/sodium acetate buffer and the other simply aqueous acetic acid (No. 2). The solid samples are crushed to pass a 9.5 mm sieve and extracted at a liquid-to-solid ratio of 20:1 in a tumbling apparatus for 18 hours. The TCLP represents to some degree a worst-case scenario as far as solid wastes are concerned.

6.2.2. Apparatus and Materials

A zero-headspace extractor (ZHE) and agitator configured for 4 samples were purchased from Associated Design and Manufacturing Co., Alexandria, VA.
Water used in preparing all the samples was first distilled and then deionized using ion exchange columns and had a conductivity of less than 10 μ ohms.

9.5 mm (3/8") size sieves used were from Soiltest Inc., 2205 Lee St., Evanston, IL

Other necessary materials were obtained from Science Supply at LSU:

- 20 mL scintillation vials with polyethylene cap, specimen cups,
- 250 mL wide mouth nalgene bottles, 2 L wide mouth nalgene bottles,
- 9 cm Whatman glass filters, membrane filters and atomic absorption standards.

6.2.3). General Procedure

The vials containing the cured samples were broken with a pestle in a mortar, the glass removed, and the cement pellet broken down into the correct size pieces. The fragments must pass through a 9.5 mm sieve. The mortar and pestle are cleaned with a 1:1 HCl/H₂O solution.

The extraction fluid No. 2, which is used for wastes that have a pH higher than 5.0 after digestion, was used for all extractions in the present cases. The extraction fluid No. 2 is prepared by diluting 5.7 mL of glacial acetic acid to 1.0 L. The solution has a pH value of 2.88 to 2.90.

The process was modified only in that the sample size was 10 g and 200 mL of extractant was used vs the actual EPA procedure, which uses 100 g samples and 2 L extractant. The liquid to solid ratio for the extraction is 20:1. A 10 g sample and 200 mL of acetic acid solution were placed in a 250 mL wide mouth bottle. Two small bottles were then placed in 2 L nalgene bottles and a foam plug inserted in the top of the large bottle to keep the smaller bottles from moving. The samples in the bottles rotated in the extractor and agitator at a single speed of 29 rpm for 18 hours. The mixture was suctioned.
filtered using glass microfiber filters in a Büchner funnel and a 250 ml filtering flask. The pH value of the filtrate was measured with a Sargent-Welch 8000 pH meter. The filtrate was acidified with 0.5 mL of concentrated nitric acid, which changes the pH from about 11-12 to about 4. In all cases a clear filtrate was obtained and no further digestion procedure was employed to remove the turbidity.

6.2.4). Metal analysis

Metal analysis was carried out on an Elan 6000 inductively coupled argon plasma spectrometer (ICAP). Sc was used as the internal standard to check for instrument drift. The instrument was calibrated using a stock Cr solution of 10, 20, 100, 500 ppb. The calibration produced a $r^2$ value of 0.999992. A 50 ppb check solution was run every 10 samples. All checks were within ± 10% as recommended.

6.3 XAS Experiments

XANES and XAFS spectra were obtained at the double-crystal monochromator (DCM) beamline at the CAMD synchrotron facility at Louisiana State University, Baton Rouge, LA.

The CAMD storage ring is designed to operate in the range of 1.2 to 1.4 GeV with respective beam currents of 400 and 200 mA. The performance, however, exceeds the specifications easily attaining an electron-beam energy of 1.5 GeV. This increases the critical photon energy to 2.6 keV and makes X-rays with energies in excess of 10 keV available from bending magnet radiation.

Standard Cr samples and simulating waste samples with cement matrix were prepared in finely ground powder for XAS analysis. All reported data were collected by fluorescence detection. The samples were placed at a 45° angle to the incident beam.
Lytle detector (EXAFS Co.) was used. The Cr K edge was calibrated at 5989 eV for analysis. The spectra were obtained by scanning the monochromator in 0.2-eV from 5933 eV to 6500 eV (about 70 eV below the edge and 500 eV above the edge), and recording the Cr Kα fluorescence intensity at each energy. Usually each energy step in the spectra was counted for 1-second live time, which yielded several thousand counts per pixel above the edge and a total scan time of approximately 45 to 60 minutes. Samples were analyzed at liquid N₂ temperature (77K ± 10K).

6.4. NMR Experiments

Solid state NMR of cement samples solidified with additives has been carried out in order to follow the development of the solid matrix during the setting of cement. The relative proportion of silicon atoms in different chemical environments in the cement matrix was examined by NMR spectroscopy.

6.4.1. Experimental Condition

Specimens were ground to a fine powder so that the mixture would pass through a 100 mesh screen and packed in zirconia rotors. Solid-state ²⁹Si MAS NMR studies were performed with a Bruker MSL-200 spectrometer. The zirconia rotors hold ~ 300 mg of solid. Samples in the rotors were spun with compressed nitrogen at a rate of 5 - 5.15 kHz. Spin rate was measured by detecting the rate of rotation of a static electrical charge on the rotor surface with a high impedance probe and measuring the frequency of rotation with a Tektronix 2465 oscilloscope.

Most of the spectra were obtained at a resonance frequency of 39.7 MHz using 5 μs 90⁰ pulses with a relaxation delay of 5 s. Two important concerns were the poor sensitivity for ²⁹Si and the long spin-lattice relaxation times for some ²⁹Si sites. The
spin-lattice relaxation times were measured by the inversion-recovery method for cement, both newly prepared samples and those aged for one year. The longest spin-lattice relaxation time found was 1.5 s. Therefore a relaxation delay of 5 s was used for all $^{29}$Si MAS NMR experiments for cement samples with an age greater than 1 day. For those samples, a signal to noise ratio of 20-40 were obtained in 6000 - 8000 scans, corresponding to 8 - 11 hours of instrument time for each sample. However, the 5 s relaxation delay was incompatible with the signal averaging requirements for the 8 h and 24 h samples, since changes in Si environments were occurring relatively fast. The following strategy was used: for the 8 h samples the relaxation delay was set to 1 s; with 5000 scans, the spectra were acquired in 1.5 h. For the 24 h samples, the relaxation delay was set to 5 s; with 2000 scans, the spectra were acquired in 3 h.

Chemical shifts are reported in ppm relative to the resonant frequency of an external standard sample of tetramethylsilane (TMS).

6.4.2). Analysis of $^{29}$Si Spectroscopic Data

A software program called “NMR1” and developed by New Methods Research Inc., of Syracuse, NY was used to analyze and integrate the solid-state NMR spectra with overlapping and poorly characterized peaks. NMR1 is a FORTRAN 77 graphics-oriented software system and runs on VAX or micro VAX computers. The free induction decays were transferred from the Bruker spectrometer to the VAX system using the transfer software Kermit, and converted to NMR1 format. The data were processed by applying baseline correction to the free induction decay. An exponential multiplication weighting function was applied using line broadening, and the data were Fourier transformed. The spectra were phased, and baseline deconvolution was applied.
to correct the spectral baseline. Peaks were analyzed using a "curve fitting" subroutine. Curve fitting is primarily used to obtain quantitative measures of the parameters (location, integrals, intensities and line widths) associated with overlapping peaks. Further details of this program are given in our earlier works\[^{111}\].

A second method "window integration" was also applied to analyze the spectra using the Bruker NMR spectrometer's own integration program. The peaks of the NMR spectra were integrated in independent windows. The integrations done with both curve-fitting using NMR1 and window integration on the Bruker NMR spectrometer were found to be in close agreement with each other\[^{80,111}\].

Generally accepted precision in NMR integration is ± 5\%\[^{111}\]. Reproducibility of spectral integrations among separately prepared samples is within the range of ± 8\%\[^{77}\].
7.1. Leaching effects of treatment by Fe(II) salts

In a previous publication\textsuperscript{[142]} we discussed the combination of the two techniques, namely reduction of Cr(VI) and simultaneous immobilization within a cement matrix, and confirmed the utility of this approach through leaching studies. Cr(III) was effectively immobilized by Type 1 Portland cement matrices, as judged by the Toxicity Characteristic Leaching Procedure (TCLP). The addition of Class F fly ash, or a variety of other additives did not compromise this good performance. Cr(VI), on the other hand, was poorly immobilized by a wide variety of cement-based binders, and increasing cure time did not significantly improve performance.

The effects of Fe(II) salts on Cr(VI) immobilization are dramatic (Table 7-a, b, c and Fig. 7-1, 7-2, 7-3). For the samples at age 28 days containing 100,000 ppm of Cr(VI) originally, the addition of FeSO\(_4\) reduces the leachability of Cr(VI) by more than 100 fold (Table 7-2 a); and FeCl\(_2\) by more than 10 fold (Table 7-2 b). The least dramatic is Fe\(_3\)O\(_4\), but it also reduces the leachability by one fourth (Table 7-2 c). The comparison is also presented in Fig. 7-1.

At the 10,000 ppm Cr(VI) level, all three iron reagents are able to control Cr leaching concentration below the TCLP regulatory limit of 5 mg/L after 28 days of cure with a 3:1 molar ratio of Fe(II):Cr(VI). At one year of age, leaching of Cr reduced with FeSO\(_4\) dramatically increased to about 21 mg/L. Form samples reduced with Fe\(_3\)O\(_4\), Cr in the leachate barely reached the 5 mg/L limit. FeCl\(_2\) appears to be the most effective...
reductant by curbing Cr leaching to around 0.1 mg/L, a lower concentration than that produced by the other two iron reagents by one order of magnitude. Also, the FeCl₂ containing matrix retains the low leachability at one year (Table 7-1 a, b and c and Fig. 7-2).

For the 1,000 mg/L Cr(VI) samples, both Fe(II) salts and Fe₃O₄ control the Cr release to less than 0.1 mg/L. FeCl₂ is again the best agent for Cr leaching control at this level. One year samples for all three agents show significantly higher concentrations of Cr in the leachates, but still a low level of leachability that would be protective of the environment (Table 7-1 a, b, c and Fig. 7-3).

Over the pH range of 2.0-10.0, aqueous Fe(II) quantitatively reduces aqueous Cr(VI). The reaction:
\[
\text{Cr}^{(VI)} (\text{aq}) + 3 \text{Fe}^{(II)} (\text{aq}) \rightarrow \text{Cr}^{(III)} (\text{aq}) + 3 \text{Fe}^{(III)} (\text{aq})
\]
was observed [2] to be complete within 1-2 minutes. At higher pH, the competitive oxidation of aqueous Fe(II) by dissolved oxygen makes the molar ratio deviate from the predicted 3.0 to a significantly higher value [2].

One of the important characteristics of the S/S process using cement or cement-like materials is the high resulting pH of the cement pore water, which is considered valuable to precipitate heavy metals conveniently. Table 7 shows that the pHs of all leachates of solidified waste samples using the stoichiometrically required amount of Fe reagents are above 7, and most of them around 12. The leaching solution is 0.04 molar acetic acid with an initial pH of only 2.9. This shows the high resulting pH for the solidified waste with cement.
Table 7-1a. TCLP Leachate Concentrations (mg/L) and pH's from Wastes Solidified with FeSO₄ Cured for 28 Days and One Year
Molar ratios of Fe(II) : Cr(VI) were 3:1 and 6:1. Blank = OPC + Fe(II). 1y = 1 year.

<table>
<thead>
<tr>
<th>Cr(VI), mg/L mixed in OPC</th>
<th>FeSO₄ 3:1</th>
<th>FeSO₄ 6:1</th>
<th>FeSO₄ 3:1(1y)</th>
<th>OPC+ Cr(VI) only</th>
<th>OPC+ Cr(III) only</th>
</tr>
</thead>
<tbody>
<tr>
<td>100,000</td>
<td>9.84</td>
<td>9.16</td>
<td>18.6</td>
<td>1400</td>
<td>0.236</td>
</tr>
<tr>
<td>Leachate pH</td>
<td>9.0</td>
<td>5.2</td>
<td>8.2</td>
<td></td>
<td>11.5</td>
</tr>
<tr>
<td>Blank pH</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>6.8</td>
</tr>
<tr>
<td>10,000</td>
<td>1.33</td>
<td>0.11</td>
<td>21.78</td>
<td>35.64</td>
<td>0.067</td>
</tr>
<tr>
<td>Leachate pH</td>
<td>12.0</td>
<td>11.7</td>
<td>11.3</td>
<td>12.3</td>
<td>12.3</td>
</tr>
<tr>
<td>Blank pH</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>12.3</td>
</tr>
<tr>
<td>1,000</td>
<td>0.084</td>
<td>0.064</td>
<td>0.12</td>
<td>0.196</td>
<td>0.014</td>
</tr>
<tr>
<td>Leachate pH</td>
<td>12.4</td>
<td>12.2</td>
<td>12.3</td>
<td>12.3</td>
<td>12.4</td>
</tr>
<tr>
<td>Blank pH</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>12.4</td>
</tr>
</tbody>
</table>
Table 7-1b. TCLP Leachate Concentrations (mg/L) and pH's from Wastes Solidified with FeCl₂
Cured for 28 Days and One Year
Molar ratios of Fe(II) : Cr(VI) were 3:1 and 6:1. Blank = OPC + Fe(II). ly = 1 year.

<table>
<thead>
<tr>
<th>Cr(VI), mg/L mixed in OPC</th>
<th>FeCl₂ 3:1</th>
<th>FeCl₂ 6:1</th>
<th>FeCl₂ 3:1(ly)</th>
<th>OPC+ Cr(VI) only</th>
<th>OPC+ Cr(III) only</th>
</tr>
</thead>
<tbody>
<tr>
<td>100,000</td>
<td>83.3</td>
<td>1.15</td>
<td>331</td>
<td>1400</td>
<td>0.236</td>
</tr>
<tr>
<td>Leachate pH</td>
<td>8.6</td>
<td>6.3</td>
<td>7.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Blank pH</td>
<td>10.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10,000</td>
<td>0.11</td>
<td>0.07</td>
<td>0.295</td>
<td>35.64</td>
<td>0.067</td>
</tr>
<tr>
<td>Leachate pH</td>
<td>12.3</td>
<td>12.0</td>
<td>11.9</td>
<td>12.3</td>
<td>12.3</td>
</tr>
<tr>
<td>Blank pH</td>
<td>12.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,000</td>
<td>0.017</td>
<td>0.018</td>
<td>0.083</td>
<td>0.196</td>
<td>0.014</td>
</tr>
<tr>
<td>Leachate pH</td>
<td>12.3</td>
<td>12.2</td>
<td>12.2</td>
<td>12.3</td>
<td>12.4</td>
</tr>
<tr>
<td>Blank pH</td>
<td>12.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 7-1c. TCLP Leachate Concentrations (mg/L) and pH's from Wastes Solidified with Fe$_2$O$_4$
Cured for 28 Days and One Year
Molar ratios of Fe(II) : Cr(VI) were 3:1 and 6:1. Blank = OPC + Fe(II). 1y = 1 year.

<table>
<thead>
<tr>
<th>Cr(VI), mg/L mixed in OPC</th>
<th>3:1</th>
<th>6:1</th>
<th>3:1(1y)</th>
<th>OPC+ Cr(VI) only</th>
<th>OPC+ Cr(III) only</th>
</tr>
</thead>
<tbody>
<tr>
<td>100,000</td>
<td>725</td>
<td>688</td>
<td>791</td>
<td>1400</td>
<td>0.236</td>
</tr>
<tr>
<td>Leachate pH</td>
<td>11.8</td>
<td>11.5</td>
<td>11.7</td>
<td></td>
<td>11.5</td>
</tr>
<tr>
<td>Blank pH</td>
<td>12.2</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>10,000</td>
<td>0.95</td>
<td>5.48</td>
<td>5.17</td>
<td>35.64</td>
<td>0.067</td>
</tr>
<tr>
<td>Leachate pH</td>
<td>12.4</td>
<td>12.1</td>
<td>12.2</td>
<td>12.3</td>
<td>12.3</td>
</tr>
<tr>
<td>Blank pH</td>
<td>12.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1,000</td>
<td>0.056</td>
<td>0.22</td>
<td>0.59</td>
<td>0.196</td>
<td>0.014</td>
</tr>
<tr>
<td>Leachate pH</td>
<td>12.4</td>
<td>12.3</td>
<td>12.2</td>
<td>12.3</td>
<td>12.4</td>
</tr>
<tr>
<td>Blank pH</td>
<td>12.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Fig. 7-1. Comparison of TCLP Leachates for OPC Containing 100,000 ppm Cr

1 --- 28d, Fe(II):Cr(VI) = 3:1
2 --- 28d, Fe(II):Cr(VI) = 6:1
3 --- 1y, Fe(II):Cr(VI) = 3:1
Cr concentration (ppm)

Fig. 7-2. Comparison of TCLP Leachates for OPC Containing 10,000 ppm Cr

1 --- 28d, Fe(II):Cr(VI) = 3:1
2 --- 28d, Fe(II):Cr(VI) = 6:1
3 --- 1y, Fe(II):Cr(VI) = 3:1

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Fig. 7-3. Comparison of TCLP Leachates for OPC Containing 1,000 ppm Cr

1 --- 28d, Fe(II):Cr(VI) = 3:1
2 --- 28d, Fe(II):Cr(VI) = 6:1
3 --- 1y, Fe(II):Cr(VI) = 3:1
Secondly, it seems difficult to perform a stoichiometric reaction in the solid or semi-solid mixture of a S/S system. For that reason a set of experiments was carried out with an overdose of Fe(II), in which the molar ratio of Fe(II):Cr(VI) is 6:1.

Over-dose Fe(II) gives encouraging results. It can decrease the leachate concentrations of FeSO$_4^-$ and FeCl$_2^-$-containing samples by one or two orders of magnitude (Table 7-1 a, b, c and Fig. 7-1, 7-2, 7-3.). And there are no extra retardation effects on the cement hydration compared to the 3:1 ratio samples at 10,000 ppm and 1,000 ppm Cr level (see 28 d samples of FeCl$_2$ and 2FeCl$_2$ in Appendix A). These results were observed despite the fact that the relatively large amounts of FeSO$_4$ and FeCl$_2$ decreased the total alkalinity of the system, as shown by the fact that the pH of the TCLP leachates was appreciably lower.

Fe$_3$O$_4$ was included in these studies as a cheap source of iron. But it is, of course, a mixture of Fe(II) and Fe(III) and thus would not be expected to be as efficient at Cr(VI) reduction as a pure Fe(II) salt. Fe$_3$O$_4$ addition does show reductions in Cr leachability compared to the system with no Fe added, but it is much poorer at reducing Cr leachability compared to FeCl$_2$ or FeSO$_4$. From the comparison of Fig. 7-1, 7-2 and 7-3, over-dose Fe$_3$O$_4$ enhances leaching of Cr compared to the 3:1 ratio. The reason is not clear. In any event, the use of Fe$_3$O$_4$ in any of these systems does not appear practical.

7-2 Sample aging and leaching effects

Another important piece of information found by the leaching study was the aging effects in this reducing-fixing S/S treatment. As can be clearly seen in Table 7-1 and Fig. 7-1, 7-2 and 7-3, the leachate concentrations of Cr are more than doubled from age 28 days to one year old for almost all samples of the three Fe additives. It is not
surprising to observe the aging effects in OPC samples, because hydration of cement is a sequence of overlapping chemical reactions leading to continuous cement paste stiffening and hardening. It is a very complex and time-consuming process, as discussed earlier. In some other work from our laboratories, increasing leachability of arsenic with increasing time of cure has been associated with matrix changes that begin to take place at long cure time. It is reasonable to expect that some types of matrix changes are occurring in the present cases, but that issue will be investigated in later work.

For comparison with the XAS study, we collected a new set of TCLP data for 3-month-setting Cr samples, which is summarized and compared to 28-day and 1-year setting samples in Table 7-2.

It is interesting that the least leachable Cr concentrations were observed at 3-month of cure for both FeSO₄ and FeCl₂ in the 10% Cr samples. Cr in the leachates dropped below 5 mg/L from about 10 mg/L for the 28-day FeSO₄ sample, and decreased about one-fourth in the FeCl₂ sample. Assuming there is a relation between Cr leachability and degree of hydration in the OPC matrix, this may be one piece of evidence for Cr products retarding early hydration of cement, which we will discuss in more detail in later chapters.

No significant change was observed in Cr concentration in leachates of the Fe₃O₄ samples from 28-day through 3-month to one year. It can be due to the chemical ineptness of Fe₃O₄ toward Cr(VI), and Cr(VI) has much less effect on cement hydration than does Cr(III).

Generally, the addition of Fe(II) compounds as the reducing reagents is very effective to stabilize Cr(VI) species in cement, but many stability and concentration
issues remain of concern, and almost all chemicals added and Cr species influence the hydration process of the cement samples, as presented in the following research and discussions.

7-3. XANES analysis and Cr speciation

Figure 7-2 demonstrates qualitatively with the pre-edge absorption peaks in the Cr XANES spectra that all three Fe(II) reagents applied in this program showed obvious chemical effects on Cr(VI), but different reductants have significantly different reducing power on Cr(VI). FeSO₄ appears most effective in reducing Cr(VI) to Cr(III), because no Cr(VI) is detectable in the spectrum. After the same curing time (28 days), there is still an appreciable amount of Cr(VI) in the sample with FeCl₂, and much more Cr(VI) existing with Fe₃O₄. This provides direct evidence for our previous report [⁹] that the effectiveness of stabilization of the Cr waste samples is closely relative to the speciation of Cr ions in it. This explains, at least chemically, why the leachability of Cr-containing samples is different with different iron reductants.

While all the three Fe(II) salts were able to decrease the Cr leachability, the reducing power is dramatically different among them. For the samples at age 28 days containing 100,000 ppm (10% wt.) of Cr(VI) originally, the addition of the stoichiometric amount of FeSO₄ reduces the leachability of Cr(VI) by about 1,000 fold at 28 days and 10,000 fold at 3 months; and FeCl₂ by about 120 fold at 28 days and 10,000 fold at 3 months. The least effective is Fe₃O₄, it reduces the leachability by less than one half (Table 2). Because of the major differences in leachability in comparisons of Cr(III) and Cr(VI) shown on the bottom of Table 7-2, it seems reasonable to relate the high leachability of Cr in the Fe₃O₄ sample to the low ability of Fe₃O₄ to reduce Cr(VI) to Cr(III). Similarly,
Table 7-2. Cr Concentration in Leachate, mg/L
TCLP Leachate from 10% Cr (wt.% ) Samples\(^1\)
Solidified with OPC

<table>
<thead>
<tr>
<th>Mole Ratio of Fe(II) to Cr(VI)</th>
<th>Sample Series 1</th>
<th>Sample Series 2</th>
<th>Average Cr Conc. in ppm</th>
<th>Age of Samples</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeSO(_4)-7H(_2)O</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.0 : 1</td>
<td>10.2</td>
<td>9.45</td>
<td>9.85</td>
<td>28 days</td>
</tr>
<tr>
<td>1.5 : 1</td>
<td>398</td>
<td>318</td>
<td>358</td>
<td>3 months</td>
</tr>
<tr>
<td>3.0 : 1</td>
<td>1.22</td>
<td>1.13</td>
<td>1.18</td>
<td>3 months</td>
</tr>
<tr>
<td>4.5 : 1</td>
<td>1.25</td>
<td>1.24</td>
<td>1.25</td>
<td>3 months</td>
</tr>
<tr>
<td>3.0 : 1</td>
<td>19.3</td>
<td>17.9</td>
<td>18.6</td>
<td>1 year</td>
</tr>
<tr>
<td>FeCl(_2)-4H(_2)O</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.0 : 1</td>
<td>84.5</td>
<td>82.1</td>
<td>83.3</td>
<td>28 days</td>
</tr>
<tr>
<td>1.5 : 1</td>
<td>330</td>
<td>399</td>
<td>364</td>
<td>3 months</td>
</tr>
<tr>
<td>3.0 : 1</td>
<td>62.7</td>
<td>59.1</td>
<td>60.9</td>
<td>3 months</td>
</tr>
<tr>
<td>4.5 : 1</td>
<td>412</td>
<td>500</td>
<td>456</td>
<td>3 months</td>
</tr>
<tr>
<td>3.0 : 1</td>
<td>290</td>
<td>373</td>
<td>331</td>
<td>1 year</td>
</tr>
<tr>
<td>Fe(_3)O(_4)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.0 : 1</td>
<td>721</td>
<td>729</td>
<td>725</td>
<td>28 days</td>
</tr>
<tr>
<td>1.5 : 1</td>
<td>1250</td>
<td>975</td>
<td>1112</td>
<td>3 months</td>
</tr>
<tr>
<td>3.0 : 1</td>
<td>820</td>
<td>915</td>
<td>868</td>
<td>3 months</td>
</tr>
<tr>
<td>4.5 : 1</td>
<td>637</td>
<td>577</td>
<td>607</td>
<td>3 months</td>
</tr>
<tr>
<td>3.0 : 1</td>
<td>823</td>
<td>758</td>
<td>791</td>
<td>1 year</td>
</tr>
<tr>
<td>OPC + 10% Cr(VI)(^2) only</td>
<td>1400 (^{[9]})</td>
<td></td>
<td></td>
<td>28 days</td>
</tr>
<tr>
<td>OPC + 10% Cr(III)(^3) only</td>
<td>0.236 (^{[9]})</td>
<td></td>
<td></td>
<td>28 days</td>
</tr>
</tbody>
</table>

\(^1\) Solid Cr and Fe salts and OPC mixed together, then water added. The water/cement ratios varied with these samples between 0.5 and 0.8, since an amount of water was added to obtain a paste of approximately the same consistency in each case.

\(^2\) Cr(VI) was added as Na\(_2\)CrO\(_4\)-4H\(_2\)O; Cr(III) was added as Cr(NO\(_3\))\(_3\)-9H\(_2\)O. The iron salts are FeSO\(_4\)-7H\(_2\)O, FeCl\(_2\)-4H\(_2\)O, and Fe\(_3\)O\(_4\).
Fig. 7-4. Cr K pre-edge absorption of OPC samples containing 10% Cr(VI) with Fe:Cr ratio of 3:1.
in these samples containing 10% Cr and a stoichiometric amount of reductant, FeCl₂ does not convert all Cr(VI) to the low Cr oxidation state and the leachability of Cr is up to dozens of times higher than for FeSO₄.

The data from the XANES analysis on the system is summarized in Table 3, which provides detailed information. Given the fact that three moles of Fe(II) are required to reduce 1 mole of Cr(VI), three moles of FeSO₄ can be successful in treatment of one mole Cr(VI) in the 10% Cr sample. Under the same conditions, three moles of FeCl₂ reduced only about 70% of one mole of Cr(VI). Increasing the FeCl₂ dosage by 50% [1:4.5 ratio of Cr(VI):Fe(II)], shows no significant improvement in reduction of Cr(VI). This may suggest a significantly different reaction mechanism between FeCl₂ and FeSO₄ in such a complex cement system, since we mix solid Cr and Fe salts and OPC cement together before the hydration reaction takes place. Certainly Cl⁻ and SO₄²⁻ interact in very different ways with the aluminate fraction during hydration.

There seem corresponding reactions for both FeCl₂ and FeSO₄ samples with the Cr(VI):Fe(II) ratio of 1:1.5, in which both reagents reduce quite precisely one half of the Cr(VI). In comparison, stoichiometrically 50% of Fe₂O₄ reacts only with about 10% Cr(VI). The chemically sufficient amount of Fe₂O₄ (1:3 ratio) did not help very much, it barely decreased 3% more of Cr(VI). The overdosed Fe₂O₄ (1:4.5 ratio) made little change in the Cr speciation. This can be one of the most important reasons for the Fe₂O₄ samples to have as high as 700 mg/L Cr leachate concentration. It is not surprising to see that Fe₂O₄ is not an efficient reagent for this S/S system. The availability of Fe(II) from Fe₂O₄ and the solubility of Fe₂O₄ are obviously lower than that of both FeCl₂ and
FeSO₄. So, it is not recommended to use Fe₃O₄ as a reductant to control Cr waste, at least in such a solid and semi-solid system.

As mentioned earlier, hydration of OPC cement is a very complex and long time process. The whole process is described as going through the following steps: a pre-induction period with a strong initial exotherm, a dormant induction period, an acceleration period with significant heat evolution, a deceleration period and long-term slow hydration period. The nature of the chemical interaction among waste metal ions, other inorganic admixtures and cement components is not well understood, although the use of water-soluble admixtures to accelerate or retard the setting of cement is a well-established practice. The rate and the degree of completion of the redox reaction between Cr(VI) and iron reductants are also very possibly influenced by the cement matrix and its hydration process. Table 3 shows that FeCl₂ could neither finish the reaction with Cr(VI) at 28 days with stoichiometrical Fe:Cr ratio, nor with 50% higher Fe:Cr ratio. On the other hand, in the sample of FeSO₄ and Cr(VI), the redox reaction can be completed at least as early as 3 hours after mixing with water.

Fig. 7-2 and Table 7-3 demonstrate that XANES is indeed a powerful and convenient tool to study the speciation of elements. It allows us to directly observe the oxidation states of metals in such a complex solid state matrix, and to do qualitative and quantitative analysis.
Table 7-3. Cr K Pre-edge Absorption Peaks and corresponding Concentrations Of OPC Samples
(10 % of Cr in OPC)

<table>
<thead>
<tr>
<th>Ratio of Cr(VI) to Fe(II)</th>
<th>Normalized peak area</th>
<th>Peak Fit Standard Error</th>
<th>Corresponding content Cr(VI) (% of total Cr)</th>
<th>Age of Sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>FeSO₄·7H₂O</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1:1.5</td>
<td>0.0991</td>
<td>0.004</td>
<td>51.2%</td>
<td>28 days</td>
</tr>
<tr>
<td>1:3.0</td>
<td>0.0028</td>
<td>0.008</td>
<td>ND</td>
<td>28 days</td>
</tr>
<tr>
<td>1:4.5</td>
<td>0.0018</td>
<td>0.010</td>
<td>ND</td>
<td>28 days</td>
</tr>
<tr>
<td></td>
<td>0.0014</td>
<td>0.004</td>
<td>ND</td>
<td>3 hours</td>
</tr>
<tr>
<td></td>
<td>0.0025</td>
<td>0.010</td>
<td>ND</td>
<td>28 hours</td>
</tr>
<tr>
<td>FeCl₂·4H₂O</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1:1.5</td>
<td>0.0963</td>
<td>0.004</td>
<td>49.7%</td>
<td>28 days</td>
</tr>
<tr>
<td>1:3.0</td>
<td>0.0550</td>
<td>0.003</td>
<td>28.4%</td>
<td>28 days</td>
</tr>
<tr>
<td>1:4.5</td>
<td>0.0447</td>
<td>0.017</td>
<td>23.1%</td>
<td>28 days</td>
</tr>
<tr>
<td>Fe₃O₄</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1:1.5</td>
<td>0.1827</td>
<td>0.004</td>
<td>90.5%</td>
<td>28 days</td>
</tr>
<tr>
<td>1:3.0</td>
<td>0.1771</td>
<td>0.003</td>
<td>87.5%</td>
<td>28 days</td>
</tr>
<tr>
<td>1:4.5</td>
<td>0.1755</td>
<td>0.017</td>
<td>86.6%</td>
<td>28 days</td>
</tr>
</tbody>
</table>

ND – Non-detectable.
8.1. Earlier Studies of Cement hydration

The reaction of cement clinker with water is exothermic. Thus, early stages of the hydration process (over the first 24h and up to a few days) can be monitored by measuring the rate of heat evolution as a function of time. Typical heat evolution processes shown schematically in Fig. 8-1, usually show two peaks. The first peak, reaching a maximum after about two to five minutes of mixing, represents the heat of wetting of the cement clinker and is mainly due to the hydration of free lime and other alkalis and the reaction of C₃A with gypsum. Thus, the first peak has been attributed to the rapid dissolution of the clinker grains to release Ca²⁺, OH⁻, SO₄²⁻, and SiO₄⁴⁻ into the liquid phase of the hydrating cement.[112, 113]

Following the initial exotherm, there is a deep valley in the heat evolution curve when little or no heat output appears for about two hours and this is referred to as the “induction” or “dormant” period. After the dormant period, a second and lower heat evolution peak appears and reaches a maximum after around 5 to 8 hours and is largely linked with the hydration of the principal clinker phase, C₃S. It is considered to be attributed to the renewed hydration of the cement grains to maintain the calcium ion concentration in the solution. Silicate hydration is believed to be the major contributor to the second peak.[114] ⁴⁹Si NMR of the cement paste during this acceleration period shows significant growth of dimeric silicate units, Q¹, at the expense of the orthosilicate units, Q⁰[111]. [H NMR relaxation time measurement[112] detect the
Fig. 8-1. The effect of admixture on heat evolution during the early hydration of OPC
presence of C-S-H gel at 6 hours. Thus, the second peak in the calorimetric curve correlates with the appearance of the C–H gel as found by the $^{29}\text{Si}$ NMR and $^1\text{H}$ relaxation time measurements.

8.2. Assessment of Accelerators and Retarders from Earlier Studies

As shown in Fig. 8-1., an additive is considered as an accelerator of hydration if it brings about an increase in the height of the second heat evolution peak relative to that of the control and the peak maximum is shifted to an earlier time \[^{96}\]. Conversely, a retarder will depress the heat evolution peak and the maximum is shifted to a later time \[^{97}\].

CrO$_4^{2-}$ has been listed among strong accelerating anions, along with Cl$^-$, Br$^-$, NO$_2^-$ etc. (Table 8-1). The list shown in Table 8-1 is based on results taken from the literature \[^{96-102}\]. The results were from extensive calorimetric studies being carried out to investigate cement admixtures.

From those thermal studies, some researchers explained that Cr species were considered as accelerators of cement hydration because Cr(VI) anion was among the soluble calcium salts \[^{63}\], and Cr(III) was detected mainly in the hydrated cement structure but not on the surface \[^{65, 103}\]. This explanation was largely based on the osmotic model. The model describes a few key points controlling the early hydration process of cement. A membrane coating of C-S-H gel with semi-permeable properties forms around the cement grains from the beginning of the “induction” or “dormant” period; the osmotic pressure is built up by the diffusion of water and solute species through the C-S-H membrane during the dormant period; the end of the dormant period is signaled by the rupture of the membrane coating of C-S-H gel under the
Table 8-1. The ranking of inorganic anions as cement accelerators or retarders of OPC and C₃S hydration [96-102]

<table>
<thead>
<tr>
<th>Ranking</th>
<th>Calcium salt solubilities</th>
</tr>
</thead>
<tbody>
<tr>
<td>Strong</td>
<td></td>
</tr>
<tr>
<td>Accelerators</td>
<td></td>
</tr>
<tr>
<td>CaCl₂</td>
<td>74.5</td>
</tr>
<tr>
<td>CaS₂O₃·6H₂O</td>
<td>100</td>
</tr>
<tr>
<td>CaBr₂</td>
<td>142</td>
</tr>
<tr>
<td>Ca(NO₂)₂·H₂O</td>
<td>45.9</td>
</tr>
<tr>
<td>CaCrO₄·2H₂O</td>
<td>16.3</td>
</tr>
<tr>
<td>Ca(NO₃)₂</td>
<td>121.2</td>
</tr>
<tr>
<td>Ca(SCN)₂</td>
<td>150</td>
</tr>
<tr>
<td>CaI₂</td>
<td>209</td>
</tr>
<tr>
<td>Ca(ClO₄)₂</td>
<td>188.6</td>
</tr>
<tr>
<td>CaSO₄</td>
<td>0.3</td>
</tr>
<tr>
<td>Weak</td>
<td></td>
</tr>
<tr>
<td>Weak</td>
<td></td>
</tr>
<tr>
<td>Retarders</td>
<td></td>
</tr>
<tr>
<td>CaF₂</td>
<td>0.0016</td>
</tr>
<tr>
<td>CaSiF₆</td>
<td>0.33</td>
</tr>
<tr>
<td>Ca₃(AsO₄)₂</td>
<td>0.013</td>
</tr>
<tr>
<td>CaB₄O₇</td>
<td>0.31</td>
</tr>
<tr>
<td>Ca₃(PO₄)₂</td>
<td>0.002</td>
</tr>
<tr>
<td>Ca(BO₂)₂·6H₂O</td>
<td>0.25</td>
</tr>
<tr>
<td>Ca₂P₂O₇</td>
<td>Insoluble*</td>
</tr>
<tr>
<td>Ca₃(BO₃)₂</td>
<td>Insoluble*</td>
</tr>
<tr>
<td>Ca₃(VO₄)₂</td>
<td>Insoluble*</td>
</tr>
</tbody>
</table>

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osmotic pressure, and subsequently renewed hydration and growth of secondary hydration products take place during the accelerating and decelerating periods [56-62].

The osmotic model implies that the rate of hydration will depend on the thickness and permeability of those membrane coatings, as well as on the ability of ion species to diffuse through them. With this in mind, Cr species were considered as accelerators because Cr(VI) anion was among the soluble calcium salts which were considered to diffuse readily through C-S-H membrane to increase internal osmotic pressure and thus facilitate the membrane rupture and renewed hydration at the end of the dormant period[63].

From the discussion above, it is clear that the “accelerator or retarder assessment” of Cr is based on the second heat evolution peak of the thermal analysis curve, which is largely due to the hydration reactions of the C₃S phase of the cement, lasting from as early as a few hours after mixing to a few days at most.

Our studies with the analysis of solid state NMR have obtained opposite results compared to the accelerator assessment of Cr discussed above. In Chapter 7, we have shown the general retarding effects of Cr(VI) and Cr(III) for the hydration of the silicate phases of OPC samples at age 28 days. In this chapter, we will continue to present the retarding effects of Cr and FeCl₂ in the samples at early age from a few hours to days.

8-3. Solid State ²⁹Si NMR Analysis

²⁹Si spectra corresponding to the hydration of cement samples at various time intervals are shown in Fig. 8-2. ²⁹Si spectra show gradual increase and decrease of peaks characteristic of the different silicates units, i.e. Q⁰ (-71 ppm) for monosilicate, Q¹ (-79 ppm) disilicates and chain end groups, Q² (-84 ppm) middle groups, Q³ (-90 ppm) chain
branching sites and $Q^4$ (-107 ppm) 3-dimensional cross-linked frameworks, during the course of hydration. The relative percent of Si atoms in different environments was determined from the NMR spectra by integrating the peak areas. The plot of Si atom percent vs. hydration time for OPC sample alone and OPC samples with Cr (VI) and Fe (II) in 1:3 mole ratio, and OPC samples with Cr (VI) and Fe (II) in 1:6 mole ratio are shown in Fig. 8-3, Fig. 8-4, Fig. 8-5 and Fig. 8-6, respectively.

Fig. 8-3 shows a steady decrease in the amount of $Q^0$ units and a significant growth in the disilicates and chain end groups $Q^1$. The $Q^0$ units become significantly less than the $Q^1$ units after 28 days. The $Q^0$ becomes less and less at a slower rate after 24 hours and does not disappear at one year.

As the hydration proceeds, $Q^1$ grows steadily and is the major component of the hydrated cement at 28 days and one year as well. The middle groups, $Q^2$, develop more slowly during the early hydration period (from 4 hours to 24 hours). The $Q^2$ units reach a maximum after 3 days and then decrease significantly until 28 days. After 28 days, the $Q^2$ units' development is stable for a long time, but then reaches a higher percent at one year. The chain branching sites $Q^3$ appear for the first time in the one year old sample.

8-4. Development of hydration process in Cr + FeCl$_2$ samples (Fe:Cr = 3:1)

The S/S system with the addition of FeCl$_2$ and Cr(VI) in the ratio of 3:1 (Fe:Cr), dramatically changes the process from that seen for OPC alone. The degree of silicate hydration is decreased from the beginning, followed by rapid hydration after about 7 days. At one year, the doped samples end up with higher proportions of hydrated silicates compared to OPC alone (Fig. 8-4).
Fig. 8-2. $^{29}$Si MAS NMR Spectra for Samples of OPC + Cr(VI) + FeCl$_2$ cured from 8 hours to one year (Fe : Cr = 3 : 1)
Fig. 8-3. Hydration Process of OPC Alone Followed by $^{29}$Si NMR
In the 3:1 (Fe:Cr) series, the sample containing 0.1% of Cr and corresponding 0.73% FeCl₂ has almost the same amount of hydrated silicates at 8h as the pure OPC paste does. Instead of accelerating the hydration of the alite or (and) other C₃S pastes, that was assumed by classic studies before, the admixture system produces a second dormant period during which the proportion of the hydrated silicates actually decreases from about 28% (at 8h for both the control and the 0.1% Cr sample) to about 15% in 7 days. During the same period, the proportion of hydrated silicates in the pure OPC (control) increases to about 60% (Fig. 8-4 and Table 8-2). After 7 days, an accelerating period shows up in the doped sample and converts the 0.1% Cr sample to approximately 100% hydration at 1 year of cure, which is a higher degree of hydration than for OPC alone.

On increasing Cr to 1.0% and FeCl₂ to 7.3%, correspondingly, the hydration reversal phenomenon occurs again from 8h to 7 days. The course of hydration development is almost the same as the sample containing 0.1% of Cr and 0.73% FeCl₂. At 7 days, it has its lowest hydration degree of about 14% (Fig. 8-4 and Table 8-3).

When the Cr is as high as 4.0% and FeCl₂ 29.2% correspondingly, the initial dehydration is not as obvious as in the 0.1% and 1.0% series. From the beginning (8h) the hydration degree of the 4.0% sample is only about 12%, which is less than one half of that in the pure OPC sample and the less-doped Cr and FeCl₂ samples (Fig. 8-4 and Table 8-4).

An interesting phenomenon is that all tested samples with Cr concentration from 0.1% to 4% show almost the same hydration degree at 7 days. The hydration degrees at that age are less than 15% and are the lowest hydration degrees for most of the samples.
Fig. 8-4. Hydration Process of OPC Containing Cr(VI) + FeCl₂ Followed by \(^{29}\)Si NMR
(Fe:Cr = 3:1)
Table 8-2. $^{29}$Si MAS NMR Chemical Shifts (ppm) and Relative Area (% in Parentheses)
For hydration processes of OPC samples containing 1,000 mg/L Cr(VI) from Na$_2$CrO$_4$ and FeCl$_2$.
For Cr(VI): % — (Atom mass of Cr/cement mass) x 100;
For FeCl$_2$: % — (Molecular mass of FeCl$_2$ / cement mass) x 100
Molar ratios of Fe(II) : Cr(VI) = 3:1

<table>
<thead>
<tr>
<th>Cr(%)</th>
<th>FeCl$_2$(%)</th>
<th>Age</th>
<th>Q$^0$</th>
<th>Q$^1$</th>
<th>Q$^2$</th>
<th>Q$^3$</th>
<th>Q$^4$</th>
<th>Hydr.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>0.73</td>
<td>8 h</td>
<td>-71.1 (71.4)</td>
<td>-78.4 (25.2)</td>
<td>-84.0 (3.4)</td>
<td>--</td>
<td>--</td>
<td>28.6</td>
</tr>
<tr>
<td>0.1</td>
<td>0.73</td>
<td>1 d</td>
<td>-71.1 (80.6)</td>
<td>-78.4 (13.7)</td>
<td>-84.0 (5.7)</td>
<td>--</td>
<td>--</td>
<td>19.4</td>
</tr>
<tr>
<td>0.1</td>
<td>0.73</td>
<td>7 d</td>
<td>-71.0 (84.8)</td>
<td>-78.4 (7.6)</td>
<td>-84.1 (5.1)</td>
<td>-90.2 (2.5)</td>
<td>--</td>
<td>15.2</td>
</tr>
<tr>
<td>0.1</td>
<td>0.73</td>
<td>28 d</td>
<td>-71.0 (39.2)</td>
<td>-78.6 (47.4)</td>
<td>-84.0 (11.1)</td>
<td>-90.2 (2.3)</td>
<td>--</td>
<td>63.8</td>
</tr>
<tr>
<td>0.1</td>
<td>0.73</td>
<td>1 y</td>
<td>--</td>
<td>-80.8 (6.6)</td>
<td>-84.8 (53.4)</td>
<td>-90.1 (40.0)</td>
<td>--</td>
<td>100</td>
</tr>
<tr>
<td>0</td>
<td>0.73</td>
<td>28 d</td>
<td>-71.1 (33.2)</td>
<td>-78.7 (39.2)</td>
<td>-84.0 (11.1)</td>
<td>-90.2 (2.5)</td>
<td>--</td>
<td>66.8</td>
</tr>
</tbody>
</table>

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Table 8-3. $^{29}$Si MAS NMR Chemical Shifts (ppm) and Relative Area (% in Parentheses)

For hydration processes of OPC samples containing 10,000 mg/L Cr(VI) from Na$_2$CrO$_4$ and FeCl$_2$.

For Cr(VI): % = (Atom mass of Cr/cement mass) x 100;

For FeCl$_2$: % = (Molecular mass of FeCl$_2$ / cement mass) x 100

Molar ratios of Fe(II) : Cr(VI) = 3:1

<table>
<thead>
<tr>
<th>Cr(%)</th>
<th>FeCl$_2$(%)</th>
<th>Age</th>
<th>$Q^0$</th>
<th>$Q^1$</th>
<th>$Q^2$</th>
<th>$Q^3$</th>
<th>Hydr.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>7.3</td>
<td>8 h</td>
<td>-71.1 (76.4)</td>
<td>-78.4 (23.6)</td>
<td>--</td>
<td>--</td>
<td>23.6</td>
</tr>
<tr>
<td>1.0</td>
<td>7.3</td>
<td>1 d</td>
<td>-71.0 (73.8)</td>
<td>-78.4 (24.5)</td>
<td>-84.0 (1.7)</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>1.0</td>
<td>7.3</td>
<td>7 d</td>
<td>-71.0 (85.9)</td>
<td>-78.4 (11.3)</td>
<td>-84.0 (2.8)</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>1.0</td>
<td>7.3</td>
<td>28 d</td>
<td>-71.1 (42.0)</td>
<td>-78.5 (36.8)</td>
<td>-83.9 (21.2)</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>1.0</td>
<td>7.3</td>
<td>1 y</td>
<td>-71.1 (4.4)</td>
<td>-80.8 (23.6)</td>
<td>-84.3 (44.8)</td>
<td>-89.9 (27.2)</td>
<td>--</td>
</tr>
<tr>
<td>0</td>
<td>7.3</td>
<td>28 d</td>
<td>-71.0 (45.3)</td>
<td>-78.6 (35.8)</td>
<td>-84.1 (13.1)</td>
<td>-90.3 (5.8)</td>
<td>--</td>
</tr>
</tbody>
</table>
Table 8-4. $^{29}$Si MAS NMR Chemical Shifts (ppm) and Relative Area
(% in Parentheses)
For hydration processes of OPC samples containing 40,000 mg/L Cr(VI)
from Na$_2$CrO$_4$ and FeCl$_2$.
For Cr(VI): % — (Atom mass of Cr/cement mass) x 100;
For FeCl$_2$: % — (Molecular mass of FeCl$_2$ / cement mass) x 100
Molar ratios of Fe(II) : Cr(VI) = 3:1

<table>
<thead>
<tr>
<th>Cr(%)</th>
<th>FeCl$_2$(%)</th>
<th>Age</th>
<th>$Q^0$</th>
<th>$Q^1$</th>
<th>$Q^2$</th>
<th>$Q^3$</th>
<th>$Q^4$</th>
<th>Hydr.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.0</td>
<td>29.2</td>
<td>8 h</td>
<td>-71.0 (87.5)</td>
<td>-78.4 (7.1)</td>
<td>-84.0 (5.4)</td>
<td>--</td>
<td>--</td>
<td>12.5</td>
</tr>
<tr>
<td>4.0</td>
<td>29.2</td>
<td>1 d</td>
<td>-71.0 (93.3)</td>
<td>-78.4 (6.7)</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>6.7</td>
</tr>
<tr>
<td>4.0</td>
<td>29.2</td>
<td>7 d</td>
<td>-70.9 (88.2)</td>
<td>-78.4 (6.0)</td>
<td>-84.0 (2.9)</td>
<td>-90.2 (2.9)</td>
<td>--</td>
<td>11.8</td>
</tr>
<tr>
<td>4.0</td>
<td>29.2</td>
<td>28 d</td>
<td>-71.0 (66.1)</td>
<td>-78.4 (26.9)</td>
<td>-84.0 (3.3)</td>
<td>-90.2 (3.7)</td>
<td>--</td>
<td>33.9</td>
</tr>
<tr>
<td>4.0</td>
<td>29.2</td>
<td>1 y</td>
<td>-71.0 (2.0)</td>
<td>-80.9 (30.0)</td>
<td>-84.1 (46.1)</td>
<td>-90.7 (31.9)</td>
<td>--</td>
<td>98.0</td>
</tr>
<tr>
<td>0</td>
<td>29.2</td>
<td>28 d</td>
<td>-71.1 (54.7)</td>
<td>-78.4 (27.2)</td>
<td>-84.0 (11.4)</td>
<td>-90.2 (6.7)</td>
<td>--</td>
<td>45.3</td>
</tr>
</tbody>
</table>

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during their hydrating process. After at least 7 days, the obvious accelerating effects take place in all samples with different concentrations of Cr and FeCl₂.

It seems that the addition of FeCl₂ and Cr (VI) (3:1) retards the hydration in the system and then reverses it for as long as 7 days during the initial period, and the degree of hydration at 7 days is independent of the concentrations over the range of 0.1% to 4% Cr and corresponding FeCl₂.

In discussions of cement hydration accelerators and retarders, little attention has been placed on events happening after about one day of cure. The implication has always been that retarders will continue to retard. Accelerators are assumed to produce a mature, fully hydrated cement paste sooner than OPC alone. Our work points out clearly that the situation is much more complex.

This is such an interesting effect that we need to explore it with Cr(VI) alone and FeCl₂ alone and FeCl₃ alone.

8.5. Development of hydration process in Cr + FeCl₂ samples (Fe:Cr = 6:1)

As reported in Chapter 7, the leachability of Cr from the 28-day samples is significantly reduced with the increase of the ratio of Fe(II):Cr(VI) from 3:1 to 6:1. In this chapter we will see that the hydration process and the matrices are also altered with the Fe(II) and Cl⁻ increase.

Similar to the situation in the samples of 3:1 of Fe:Cr shown in Fig. 8-4., Fig. 8-6 shows that the hydration process is retarded at least for the early period before 28 days.
with the increased amount of FeCl₂. But, after a year of cure, the hydration degree is higher than the pure OPC samples and about the same as that in the 3:1 series samples.

At one year, the hydrated silicates in all double-doped FeCl₂ are above 90%, compared to 85% in the control OPC (Fig. 8-6, Fig. 8-7 and Table 8-5).

The 0.1% Cr sample with 1.46% FeCl₂, which corresponds to double the amount of FeCl₂ over the 3:1 molar ratio required for the stoichiometric redox reaction, shows a dramatic decrease in the hydration degree from ~28% to ~9% at 8 hours. This period corresponds to the second peak of heat release on the thermal analysis curve (Fig 8-1). Proceeding to 1 day and 7 days, the hydration degrees are still significantly lower than that of the pure OPC sample, but higher than that in samples containing a smaller amount of FeCl₂ (0.73% in 3:1 series) (Fig. 8-6, 8-7a and Table 8-5).

The samples with the higher ratio of Fe(II) to Cr(VI) do not show the peculiar reversal (or at least stagnation) of hydration between 8h and 7 days that was observed in the 3:1 (Fe:Cr) samples. With the higher proportion of FeCl₂ the early hydration is greatly diminished, but then steadily catches up and eventually overtakes the hydration of OPC alone.

It is clear that the addition of FeCl₂ and Cr salts (both 6:1 and 3:1) reduces the hydration degree of the OPC cement during the whole critical early hydrating period from hours to days. It is not clear, however, why the double amount (1.46%) of FeCl₂ showed the obviously stronger retarding effect at 8 hours compared to the stoichiometric amount (0.76%) of FeCl₂, but a smaller retarding effect at 1 day and 7 days. Ultimately, there is no significant difference between the 6:1 and 3:1 samples at 28 days and one year in the portion of the hydrated silicates (Fig 8-7a).
Fig. 8-5. $^{29}$Si MAS NMR Spectra for Samples of OPC + Cr(VI) + FeCl$_2$ cured from 8 hours to 28 days (Fe : Cr = 6 : 1)
Fig. 8-6. Hydration Process of OPC Containing Cr(VI) + FeCl₂ Followed by $^{29}$Si NMR
(Fe:Cr = 6:1)

- Control — OPC alone
- 0.1% Cr + 1.46% FeCl₂
- 1.0% Cr + 14.6% FeCl₂
- 4.0% Cr + 58.4% FeCl₂

Hydration Degree (%) = (Hydrated Silicates / Total silicates) × 100

Hours (h)
Fig. 8-7a. Comparison of Hydration Process of OPC and OPC Samples Containing 0.1% Cr(VI) with Different Fe:Cr Ratio of 3:1 and 6:1

1. 8 hours.
2. 1 day.
3. 7 days.
4. 28 days.
5. 1 year.
Fig. 8-7b. Comparison of Hydration Process of OPC and OPC Samples Containing 1.0% Cr(VI) with Different Fe:Cr Ratio of 3:1 and 6:1
Fig. 8-7c. Comparison of Hydration Process of OPC and OPC Samples Containing 4.0% Cr(VI) with Different Fe:Cr Ratio of 3:1 and 6:1

1. 8 hours.
2. 1 day.
3. 7 days.
4. 28 days.
5. 1 year.
Table 8-5. $^{29}$Si MAS NMR Chemical Shifts (ppm) and Relative Area (% in Parentheses)

For hydration processes of OPC samples containing Cr(VI) and FeCl$_2$.
For Cr(VI): % — (Atom mass of Cr/cement mass) x 100;
For FeCl$_2$: % — (Molecular mass of FeCl$_2$ / cement mass) x 100
Molar ratios of Fe(II) : Cr(VI) = 6:1

<table>
<thead>
<tr>
<th>Cr(%)</th>
<th>FeCl$_2$(%)</th>
<th>Age</th>
<th>Q$^0$</th>
<th>Q$^1$</th>
<th>Q$^2$</th>
<th>Q$^3$</th>
<th>Q$^4$</th>
<th>Hydr.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>1.46</td>
<td>8 h</td>
<td>-71.1 (90.6)</td>
<td>-78.5 (7.4)</td>
<td>-84.0 (2.0)</td>
<td>--</td>
<td>--</td>
<td>9.4</td>
</tr>
<tr>
<td>0.1</td>
<td>1.46</td>
<td>1 d</td>
<td>-71.1 (74.1)</td>
<td>-78.5 (19.3)</td>
<td>-84.0 (6.6)</td>
<td>--</td>
<td>--</td>
<td>26.1</td>
</tr>
<tr>
<td>0.1</td>
<td>1.46</td>
<td>7 d</td>
<td>-71.0 (54.3)</td>
<td>-78.6 (32.3)</td>
<td>-83.6 (9.1)</td>
<td>-90.1 (3.3)</td>
<td>--</td>
<td>45.7</td>
</tr>
<tr>
<td>0.1</td>
<td>1.46</td>
<td>28 d</td>
<td>-71.1 (37.3)</td>
<td>-78.8 (43.4)</td>
<td>-84.0 (13.3)</td>
<td>-90.2 (3.8)</td>
<td>-107.6 (2.2)</td>
<td>62.7</td>
</tr>
<tr>
<td>1.0</td>
<td>14.6</td>
<td>8 h</td>
<td>-71.1 (96.9)</td>
<td>-78.5 (3.1)</td>
<td></td>
<td></td>
<td>--</td>
<td>3.1</td>
</tr>
<tr>
<td>1.0</td>
<td>14.6</td>
<td>1 d</td>
<td>-71.2 (89.0)</td>
<td>-78.5 (7.9)</td>
<td>-84.0 (3.1)</td>
<td>--</td>
<td>--</td>
<td>11.0</td>
</tr>
<tr>
<td>1.0</td>
<td>14.6</td>
<td>7 d</td>
<td>-71.0 (78.7)</td>
<td>-78.5 (14.9)</td>
<td>-84.0 (3.9)</td>
<td>-90.2 (2.5)</td>
<td>--</td>
<td>21.3</td>
</tr>
<tr>
<td>1.0</td>
<td>14.6</td>
<td>28 d</td>
<td>-71.1 (48.1)</td>
<td>-78.5 (31.6)</td>
<td>-84.0 (20.0)</td>
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<td>-107.6 (1.7)</td>
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</tr>
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<td>4.0</td>
<td>58.4</td>
<td>8 h</td>
<td>-71.3 (93.7)</td>
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<td></td>
<td></td>
<td>--</td>
<td>6.3</td>
</tr>
<tr>
<td>4.0</td>
<td>58.4</td>
<td>1 d</td>
<td>-71.2 (94.3)</td>
<td>-78.5 (5.7)</td>
<td></td>
<td></td>
<td>--</td>
<td>5.7</td>
</tr>
<tr>
<td>4.0</td>
<td>58.4</td>
<td>7 d</td>
<td>-71.0 (92.2)</td>
<td>-78.5 (4.7)</td>
<td>-83.7 (3.1)</td>
<td></td>
<td>--</td>
<td>7.8</td>
</tr>
<tr>
<td>4.0</td>
<td>58.4</td>
<td>28 d</td>
<td>-71.0 (80.7)</td>
<td>-78.5 (19.3)</td>
<td></td>
<td></td>
<td>--</td>
<td>19.3</td>
</tr>
</tbody>
</table>
In the samples containing 1.0% Cr, there is a similar pattern to that in the 0.1% Cr samples. The admixtures of FeCl₂ and Cr in both 6:1 and 3:1 systems decrease the hydration degree from 8 hours to 28 days. The larger amount of FeCl₂ (14.6%) shows dramatic retarding effects at 8 hours compared to the stoichiometric amount (7.6%) of FeCl₂, and is also more retarding compared to the 3:1 sample at 1 day, which is a longer retarding period than that in the 0.1% Cr + 1.46% FeCl₂ system. But, at 7 days the 3:1 sample has caught up as it did in the 0.1% Cr samples (Fig. 8-7b).

In comparison within the 6:1 system, it is very clear that the samples of 1.0% Cr with 14.6% FeCl₂ have significantly stronger retarding effects than the samples of 0.1% Cr with 1.46% FeCl₂ from 8 hours to 28 days (Fig. 8-6). This is another clear evidence that Cr and FeCl₂ are retarders for OPC hydration.

When the content of Cr is as high as 4%, with 58.4% FeCl₂ in the 6:1 series, and 29.2% FeCl₂ in the 3:1 series, respectively, the retarding effects are very obvious during the entire early hydration period up to 28 days. The hydrated silicates remain below 10% for about the first 7 days, which is around one fifth of the amount of hydrated silicates observed in the OPC samples without the admixtures. In this high Cr-content system, more FeCl₂ results in stronger retardation (Fig. 8-6, 8-7c).

8.6 Discussion of the Interaction Mechanism of Cr Wastes with the Cement Matrix

The combination of calorimetric studies and the osmotic model has been used to show that chromate is an accelerator for cement hydration and to offer an explanation. There are also other studies implying support to the assessment.
Calorimetric work has not been reported on Cr(III)-doped cements. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) analysis have led to the conclusion that Cr (III) species is chemically incorporated inside the cement structure. Fourier transform infrared spectroscopy (FTIR) and energy dispersive spectroscopy suggest that either the Cr(III) ions have been incorporated within the C-S-H, or the polymerization of the silicates has been affected by the reaction and/or adsorption of chromium on the components of hydrating OPC. Particularly, X-ray photoelectron spectroscopy (XPS) surface detection finds the striking difference between the surface concentration of Cr- and Pb-doped samples. The very small signal-to-noise for Cr suggests that the Cr is located below the 15 or so angstrom depth probed by the XPS technique. These modern analytical tools imply that the Cr functions totally differently from Pb waste, which is considered as a retarder in a consensus of opinion.

From the $^{29}$Si NMR analysis of Cr(VI) and Cr(III) samples presented in Chapter 7, and the Cr + FeCl$_2$ system in this chapter, and more data for Cr + FeSO$_4$ to be shown later, we have found that the structure of the cement matrix is significantly modified by Cr, especially Cr(III), and we have observed strong retardation effects of the Cr and Fe salts in the hydrating cement paste. Therefore, we disagree with the common assessment that Cr(VI), Cr(III) and chloride can be expected to be accelerators in most, if not all, circumstances.

Pb is a known hydration retarder and primarily a surface species in cement paste. The osmotic model explains well the relation between the retarding effect and the surface species status of Pb, because, in contrast to Cr, Pb forms insoluble salts on the
top of hydrating cement particles \[6^3, 7^1\] resulting in a diffusion barrier to water to slow the rate of hydration.

It is incorrect, however, to assess that both Cr(VI) and Cr(III) are accelerators with this model. Cr(VI) species are much more soluble than Cr(III), but all reports of detection of incorporation of Cr inside the cement structure by SEM, TEM, FTIR and EDS are for Cr(III). It has not been shown by instrumental analysis that the soluble Cr(VI) can migrate through the C-S-H membrane and incorporate into the inside structure of hydration products, as would be suggested by solubility arguments applied to the osmotic model.

Cr(III) produces very insoluble Cr(OH)\(_3\) and other Cr(III) coprecipitates at pH 6 and higher \[2^5\] (Chapter 2), which is the normal condition in hydrating cement and the precipitation/dissolution kinetics of Cr(OH)\(_3\) are rapid \[2^5\]. Therefore, it is fair to say that Cr(III) is able (as much as Pb) to form a dense coating or diffusion barrier at the very beginning of C-S-H hydration and also less likely to penetrate into the inside structure of C-S-H gel, as suggested by the osmotic model solubility arguments.

It is evident that both Cr and Pb retard the cement hydration process during the early development of hydrated silicates. But, if the control key factor of the mechanism for Pb retardation is the formation of a diffusion barrier, the one for Cr must be something else and something subject to further research.

A significant increase in compressive strength is found for both Cr(VI)- and Cr(III)-contained cement samples \[6^7, 7^2, 7^3\]. For Cr(III) additives, it was explained as a result of the formation of Cr(OH)\(_3\)\(-n\)H\(_2\)O gel \[7^2\] which has properties similar to C-S-H gel. If that is the case, replacement of C-S-H gel with Cr(OH)\(_3\)\(-n\)H\(_2\)O gel takes place, since our
observations show significant decrease of hydrated silicates in the samples. For Cr(VI), it was said that the formation of chromate by the reaction of \( \text{CrO}_4^{2-} \), with \( \text{Ca}^{2+} \), \( \text{K}^+ \), and \( \text{Na}^+ \) ions, results in the increased hydration of the cement matrix. It is clear that the outcomes of our research are completely opposite to this explanation, because the hydration is always deceased by the addition of \( \text{CrO}_4^{2-} \).

There is another interesting issue for Cr S/S study. Researchers pay a lot of attention to the effects of waste elements on the cement matrix. It is commonly considered that if the development of C-S-H gel is adversely affected by the wastes with retarded hydration, then lower mechanical strength and higher leachability of the waste elements may be expected. This is, however, not the case in the Cr treatment S/S system, where there is early retardation, but ultimately improved compressive strength and low (at least for Cr(III)) leachability.

Our work shows that Cr(VI) has significant less retardation effect, hence less modification effects on the structure of cement matrix than Cr(III), but much higher leachability. It may imply that the mechanism for the S/S system with OPC to immobilize Cr wastes is likely a chemical one rather than something else dependent on physical strength of the cement matrix.

8-7. Polymerization of Hydrating silicates in Cr + FeCl₂ samples (Fe:Cr = 3:1)

As mentioned earlier in this chapter, there is a second “dormant” period in the early hydration in the 3:1 (Fe to Cr) samples from 8 h to 7 days. During the period, contrasted to the sample of OPC alone in which the monosilicate decreases from ~70% to ~40%, the samples of the 0.1% and 1.0% series of Cr(VI) + FeCl₂ show the unhydrated silicate, \( Q^0 \), increased from ~70% to ~85%. This is actually a reversal of hydration.
In the 4.0% Cr sample, the reversal is also detectable in the early hydration although it is not so obvious as in the sample with the lower portion of Cr(VI) and FeCl₂. At 28 days, the gap in the amount of the unhydrated silicates between the OPC alone and the samples of the 0.1% Cr and 1.0% Cr is dramatically narrowed from ~35% at 7 days to less than 10%, while the 4.0% Cr still keeps ~30% higher monosilicates (Fig. 8-8a, Table 8-2 to 8-4). In the whole hydrating course of one year, the orbits of evolution of the unhydrated silicates for the 0.1% Cr + 0.73% FeCl₂ and the 1.0% Cr + 7.3% FeCl₂ are very similar, so it seems that over this concentration range of the additives of Cr(VI) and FeCl₂, the strength of effects of them on the hydration process are not significantly different. The sample with higher portion of the 4.0% Cr and corresponding 29.2% FeCl₂ has obvious higher unhydrated silicates during the most of the period.

The hydration reversal is mainly at the cost of the dimer and chain-end silicates, Q¹, for the Cr-containing samples from 8 hours to 7 days. At 8 hours, more than 20% of silicates in the series of the 0.1% Cr and 1.0% Cr has become dimer silicates or chain-ending group by hydration reaction in cement, which is almost the same amount as in the OPC alone, if not higher. After 7 days, more than one half of the dimers downgrades to monosilicates. During the same period, the OPC alone develops the dimer silicates from ~20% to ~50%. This dramatic matrix difference shows the obvious retarding or even reversing effects of the additives of Cr and FeCl₂ salts on cement hydration. It is much stagnant for the development of the disilicates in the 4%Cr series from 8h to 7 days, only ~7% dimers appears for the whole 7 days, which indicates stronger retarding in cement hydration by the higher portion of the additives. From 7 days, there is an
accelerating formation of dimer or chain-ending silicates, and it peaks at 28 days. This phenomenon happens for all 3:1 samples (Fig. 8-8b). The decrease of the dimers after 28 days does not mean the hydration reversal again, because the monosilicates continue to disappear and more dimer becomes higher degree polymers of silicates.

Before the 7th day, the additives of Cr and FeCl₂ depressed the development of higher polymers of silicates compared to the OPC alone. Much lower portion of middle and internal groups of silicates, Q², is observable in Fig. 8-8c in all Cr samples. After 28 days, more and more higher polymers are produced with the decrease of the monosilicate and the disilicates. The additives accelerate the higher polymerization after 28 days, and the Q² groups became the largest portion of the silicates at one year of cure, while the dimer, Q¹, is the largest in the OPC alone sample with the same age (Fig. 8-3 and 8-8d).

In the one-year-old sample of the OPC alone, 6% of silicates develops into chain-branching group, Q³. In the Cr(VI) + FeCl₂ system, Q³ appears much earlier from 7 days of the hydration and becomes much higher proportion of ~30% to ~40% in one year.

In summary, the addition of the Cr(VI) + FeCl₂ retards the early cement hydration until 7 days, but it promotes the higher polymerization of silicates in the hydrating paste after 28 days and makes the silicate polymers (higher than dimer) become the dominant portion in long-term of cure.
Fig. 8-8a. Distribution of Monosilicates, $Q^9$

in Hydrating OPC and OPC + Cr(VI) + FeCl₂
Followed by $^{29}$Si NMR
(Fe:Cr = 3:1)
Fig. 8-8b. Distribution of Disilicates, Q
in Hydrating OPC and OPC + Cr(VI) + FeCl
Followed by $^{29}$Si NMR
(Fe:Cr = 3:1)
Fig. 8-8c. Distribution of Middle Groups, Q^2 in Hydrating OPC and OPC + Cr(VI) + FeCl₂ Followed by ^29Si NMR (Fe:Cr = 3:1)
Fig. 8-8d. Distribution of Chain-branching, $Q^3$ in Hydrating OPC and OPC + Cr(VI) + FeCl$_2$ Followed by $^{29}$Si NMR (Fe:Cr = 3:1)
8.8. Polymerization of Hydrating silicates in Cr + FeCl₂ samples (Fe:Cr = 6:1)

There is no hydration reversal shown up for the higher portion (Fe:Cr = 6:1) samples during the early hydration. The reason is probably that the unhydrated silicates, $Q^0$, is still too much at 8 hours (more than 90%, Fig. 8-9a) and there is no enough hydrated dimers, $Q^1$, (less than 10%, Fig. 8-9b) available to decompose. The stagnant period from 8h to 7 days still exists in the samples except the 0.1% Cr system. The developments of decrease of the monosilicate and increase of the dimer-type silicates are smoother in the 6:1 samples than that in the 3:1 samples, and like the latter, the 6:1 samples end up with lower proportion of the disilicates at one year compared to the control. The retarding effects are stronger in the 6:1 samples than in the 3:1 samples for the 4.0% and the 1.0% Cr, respectively, for the most of time during the one year of cure, but it is somehow weaker for the 0.1% Cr sample of the 6:1 series before 28 days.

The developments of the higher degree polymerization of hydrated silicates are pretty similar in the 6:1 samples and in the 3:1 samples. The growth of the middle and internal groups, $Q^2$, is depressed before 7 days and accelerated after 28 days, and the $Q^2$ groups becomes the largest portion of the silicates in one year samples (Fig. 8-9c).

The distribution and the development of the chain-branching silicates, $Q^3$, are also similar for both the 6:1 and the 3:1 series. The formation of the higher polymers are enhanced by the addition of the mixture of Cr(VI) and FeCl₂, and the proportion of the higher polysilicates are dramatically higher than that in the sample of the OPC alone (Fig. 8-9d).
Fig. 8-9a. Distribution of Monosilicates, $Q^1$

in Hydrating OPC and OPC + Cr(VI) + FeCl$_2$

Followed by $^{29}$Si NMR

($Fe:Cr = 6:1$)
Fig. 8-9b. Distribution of Disilicates, $Q^1$
in Hydrating OPC and OPC + Cr(VI) + FeCl$_2$
Followed by $^{29}$Si NMR
(Fe:Cr = 6:1)
Fig. 8-9c. Distribution of Middle Groups, $Q^2$ in Hydrating OPC and OPC + Cr(VI) + FeCl$_2$ Followed by $^{29}$Si NMR
(Fe:Cr = 6:1)
Fig. 8-9d. Distribution of Chain-branching, $Q^3$ in Hydrating OPC and OPC + Cr(VI) + FeCl$_2$ Followed by $^{29}$Si NMR
(Fe:Cr = 6:1)

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8.9. Mechanism of Silicate Hydration in Cement Paste

8.9.1. Phenomena in OPC and Cr(VI)-FeCl₂-Doped OPC Samples

When OPC clinker is mixed with water the C₃A reacts rapidly, the C₃S reacts progressively, and the other phases contribute as well, resulting in a marked increase in temperature and irreversible stiffening, and a release of Ca²⁺, OH⁻, Al(OH)₄⁻, SO₄²⁻ and SiO₄⁴⁻ into the liquid phase from the clinker grains, followed by quick setting [50, 115].

The initial exotherm in the heat evolution curve (Table 8-1) is followed by low heat output for about 2 hours (induction or dormant period). After 2 hours, a second exotherm (second peak) is observed in the calorimetric curve which lasts about 8 hours into the hydration and is attributed to the renewed hydration of the cement grains. Silicate hydration is believed to be the major contributor to the second peak. ²⁹Si NMR of the cement paste during this acceleration period (8 hours) shows significant growth of dimeric silicate units Q¹ at the expense of the monosilicate units Q⁰ in the sample of OPC alone (Fig. 8-3). But in the samples with the admixtures of Cr(VI) and FeCl₂, ²⁹Si NMR shows significant stagnancy of the growth of the disilicate units Q¹ during the early period (from 8 hours to 7 days) (Fig. 8-8b and Fig. 8-9b).

Calorimetry shows a decrease in heat output (deceleration period) from 8 hours to 12 hours due to the slow hydration of the anhydrous silicate grains because diffusion through the built-up layer of C-S-H gel becomes the rate controlling step. After 16 hours, ²⁹Si NMR shows a significant decrease in the Q⁰ units and a gradual growth of Q¹ and Q² units in the sample of OPC alone. In OPC with Cr and FeCl₂, ²⁹Si NMR shows a significant increase in the Q⁰ units and no growth of Q¹ and Q² units in the 3:1
series until 7 days, and a much slower decrease in the $Q^0$ units and a stagnant growth of $Q^1$ and $Q^2$ units in the 6:1 series until 7 days (Fig. 8-8 and Fig. 8-9).

In long term samples (one year of curing), $Q^1$ units are no longer the dominant component in both the 3:1 series and the 6:1 series. $Q^2$ units take the position as the species of highest proportion in cement matrix, and significant amount of $Q^3$ and $Q^4$ units are found.

8.9.2). Models for Early hydration of Portland Cement and Discussion

The hydration and setting chemistry of Portland cement is a very active area of investigation and much remains to be learned. Several mechanisms for early hydration of C$_3$S in the cement have been proposed in past decades. In general terms, they can be divided into two categories:

1. The osmotic model (or gel model, or protective coating model).
2. The crystalline model (or delayed nucleation model).

We have had discussions of the osmotic model earlier. There are probably aspects of both models that have to be considered in detailed cement hydration and setting.

In the crystalline model, the induction period is attributed to the delay in nucleation of calcium hydroxide or C-S-H or both. The composition of the liquid phase of the hydrating C$_3$S has been studied $^{[115, 116]}$. The ionic product $[Ca^{2+}][OH^-]^2$ was calculated as a function of time and the results confirmed that the maximum Ca$^{2+}$ ion concentration corresponds to the end of the induction period and coincides with the onset of initial nucleation of Ca(OH)$_2$. A mechanism suggested by Young, et al, $^{[115]}$ is as follows:

Initial hydrolysis:
\[ C_3S + H_2O \rightarrow 'C_2S' + Ca^{2+} + OH^- \]

('C_2S' is a lime-deficient C_3S structure)

\[ 'C_2S' + H_2O \rightarrow 2 Ca^{2+} + H_2SiO_4^{2-} + 2OH^- \]

\[ H_2SiO_4^{2-} + 2OH^- \rightarrow Si_2O_7^{6-} + 2H_2O \]

At the end of the induction period:

\[ Ca^{2+} + OH^- \rightarrow Ca(OH)_2 \]

\[ SiO_4^{2-} + H_2O \rightarrow Si_2O_7^{6-} + 2OH^- \]

\[ \downarrow \text{polymerization} \]

\[ [SiO_3]_n^{2-} + 2nOH^- \]

The initial nucleation and growth of crystals of Ca(OH)_2 is very important in the crystal model. It is found \[^{114}\] that Ca^{2+} and OH^- ions are released into the surrounding water at a constant rate during the induction period, followed by a brief period of slower release (5-6 hours). Further hydration is retarded by the high Ca^{2+} ion concentration in the interfacial region (between the surface of the calcium deficient C_3S grain and the liquid phase), which results in a solution rich in Ca^{2+} and OH^- ions until sufficient supersaturation (1.5 - 2.0 times the saturation value) accumulates to give stable calcium hydroxide nuclei \[^{116}\]. At this point, a sudden drop in calcium ion concentration occurs due to the formation of calcium hydroxide and C-S-H gel \[^{114}\], which marks the end of the induction or dormant period. Then, the C-S-H gel grows outward from the cement grains in the form of needles. By about 12 hours, they eventually come into contact with other needles from other cement grains, begin to coalesce, and produce sheets of tobermorite. This coincides with the second peak of heat evolution and corresponds approximately to the completion of setting \[^{50}\].

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In the samples with admixture of Cr(VI) and FeCl$_2$, the dormant period is protracted so much that it lasts about 7 days; or, a second dormant period is produced from 8 hours to 7 days. Significant amounts of Cr(III), Fe(III) and chloride ions should be present after addition of Cr(VI) and FeCl$_2$ into the Portland cement. It is logical to consider that Cr(III) or Fe(III) or chloride, or all of them, contribute to the significantly longer dormancy or stagnancy in the early hydration.

As discussed in Chapter 7, in this treatment system of S/S and redox reaction, AFm phases, Fe(OH)$_3$, Cr(OH)$_3$ or (Cr$_x$Fe$_{1-x}$)(OH)$_3$ are most likely produced. The significant amount and insolubility of species like (Cr$_x$Fe$_{1-x}$)(OH)$_3$ can provide a strong protective coating on cement grains to delay the onset of major hydration, in terms of the osmotic model.

Regarding the crystalline model, the formation of the species like (Cr$_x$Fe$_{1-x}$)(OH)$_3$ and AFm phases, and Fe(OH)$_3$ in the samples with a high portion of admixtures, needs to consume large amount of hydroxyl. That causes competition for OH$^-$ away Ca$^{2+}$ during the induction period. The lower availability of OH$^-$ should delay the nucleation of Ca(OH)$_2$ and extend the induction or dormant period.

It is found that the morphology of C-S-H formed in the period of ~ 3h to ~ 24h is affected by Cl$^-$ among other foreign ions. However, we do not observe any accelerating effect of chloride like some other researchers (Table 8-1). Chloride may play a role in the decomposition of the early hydration product of dimeric silicate (Si$_2$O$_7^{6-}$, Q$^1$) back to monosilicate (SiO$_4^{4-}$, Q$^0$) from 8 hours to 7 days, and in the higher degree of polymerization of Q$^3$ and Q$^4$ in later hydration. This is a subject remaining unclear.
In short, based on the experimental data from $^{29}\text{Si} \text{NMR}$ and the theoretical discussion of the cement chemistry above, we found more reasons for us to expect Cr(VI), Cr(III) and FeCl$_2$ to be retarders rather than accelerators in cement hydration.

8.9.3). Polymerization of Hydrating Silicates

The structure of the silicate anions has been determined from the kinetics of the reaction with molybdate $^{[117]}$, and by trimethylsilylation (TMS) $^{[118]}$ and $^{29}\text{Si} \text{NMR}^{[74,75]}$. In TMS methods, the sample is treated with a reagent that converts the silicate anions into the corresponding silicic acids, which then react further with replacement of SiOH by SiOSi(CH$_3$)$_3$. The resulting TMS derivatives can be identified and semiquantitatively determined by various procedures.

Most of the investigations on C$_3$S pastes hydrated for more than a few hours at 15-25°C have shown that the monomer (SiO$_4^{4-}$) present is attributable to unreacted C$_3$S, and that the products formed during the first few days contain dimer (Si$_2$O$_7^{6-}$), which is first supplemented, and later replaced by larger species, collectively called polymer. The percentage of the silicon present as dimer passes through a maximum at about 6 months, but even after 20-30 years is still around 40% $^{[50]}$.

Early silicate hydration (OPC alone):

\[
\begin{align*}
\text{O}^- & \quad \text{Si} \quad \text{O}^- \quad + \quad \text{H}_2\text{O} \quad \rightarrow \quad \text{O}^- & \quad \text{Si} \quad \text{OH}^- \quad + \quad \text{OH}^-
\end{align*}
\]

monosilicate unit, $Q^0$
$^{29}\text{Si NMR}$ studies by outside researchers\textsuperscript{[74, 75]} are in agreement with our earlier work (Fig. 8-3). For C\textsubscript{2}S pastes, the content of Q\textsuperscript{0} begins to decrease after a few hours, with formation of Q\textsuperscript{1}, later accompanied by Q\textsuperscript{2}. No Q\textsuperscript{3} or Q\textsuperscript{4} is detected. This result is compatible with the formation of dimer, later accompanied or replaced by either single chains or rings, but not with that of double chains, clusters or other more complex species.

Our early work indicates that dimeric silicate Q\textsuperscript{1} greatly increased over the period from 24 hours to 3 days. During this early period, Q\textsuperscript{1} units grow at the cost of Q\textsuperscript{0} units. But after 3 days, Q\textsuperscript{1} continues to grow at the cost of Q\textsuperscript{2} instead of Q\textsuperscript{0}. Therefore, it is suggested that at late stages (after 3 days) depolymerization of Q\textsuperscript{2} units by the Q\textsuperscript{0} units takes place to give more Q\textsuperscript{1} units\textsuperscript{[111]}. After 28 days, Q\textsuperscript{1} is the major component of the cement matrix. It is also reported\textsuperscript{[120]} by $^{29}\text{Si NMR}$ that C\textsubscript{2}S was less than 20% hydrated.
after 7 days in contrast to $C_3S$ and cement samples, which were more than 50% hydrated. With this in mind, it is suggested that the cement clinker initially is predominantly $C_3S$, but as the hydration proceeds it becomes enriched in $C_2S$. And, at later stages the $Q^0$ units of $C_2S$ are involved in the depolymerization of $Q^2$ units to form more $Q^1$ units.

Later silicate hydration (OPC alone, after 3 days):

That is obviously not the case in the samples with the admixtures of Cr and FeCl$_2$. First, the dimeric silicate $Q^1$ units do not grow steadily upward. Decomposition of dimer to monosilicate takes place in many of the Cr and FeCl$_2$-doped in the early period before 7 days.
Early decomposition (doped sample):

\[
\begin{align*}
O^- - Si^- - O^- + X^- \rightarrow O^- - Si^- - O^- + O^- - Si^- - X^- \\
Q^1 \text{ unit } (x = OH^+, Cl^-, \text{etc.}) \quad Q^0 \quad Q^0
\end{align*}
\]

Second, at later stages (after 3 or 7 days), no depolymerization of \(Q^2\) or higher \(Q\) units is observable, but polymerization to form \(Q^3\) and \(Q^4\). So, if the monosilicates (SiO$_4^{4-}$) in C$_2$S join the process of hydration, they take part in polymerization of hydrated silicates rather than depolymerization.

Third, \(Q^1\) units are not the dominant component in long-time cured samples in the Cr and FeCl$_2$-doped samples. \(Q^1\) units decrease again after the increase between 7 days and 28 days of curing. \(Q^2\) units are most abundant in all doped samples, and large amounts of \(Q^3\) and \(Q^4\) units (20 ~ 40\%) are observed in the one-year-old samples.

From GLC, GPC, mass spectrometry and chemical analysis of TMS derivatives$^{[50]}$, it is concluded that the silicate anions are linear in Portland cement. Pentamer (Si$_5$O$_{16}$, negative charge and any attached hydrogen atoms are omitted) is the most important single component at all ages, and the next most important is probably linear octamer (Si$_8$O$_{23}$). As the cement paste ages, the mean size of the anions increases, and after all the C$_3$S has reacted this process continues. At 20 ~ 30 years, the pentamer and octamer consist of large portions of polymers, and larger anions with some tens of SiO$_4$ tetrahedra are also present$^{[119]}$. 

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Silicate linear chain of the type present in tobermorite and jennite:\(^{50}\):

The existence of a significant amount of chloride in the doped samples may be one of the important reasons for the early decomposition of the disilicates and for later complex polymerization:
Later polymerization (doped sample):

\[ \text{branching silicate, } Q^3 \]

\[ \text{cross-linking silicate, } Q^4 \]

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8-10. Comparison of OPC Samples Containing FeCl₂-only, Cr(NO₃)₃ only and Cr(VI) + FeCl₂ doped at 28 days and 1 year

In the previous parts of this chapter, we have discussed the OPC samples of Cr(VI) treated by mixing Cr(VI) with FeCl₂ to have a redox reaction converting Cr(VI) to Cr(III). Significant changes in the cement matrix have been observed in those samples. Here we will explore the influence of FeCl₂ salt alone on the cement hydration and matrix structure of the hydrated cement paste at 28 days and one year of cure.

We have concluded that the addition of compounds of Cr(VI) + FeCl₂ at various levels retards the cement hydration during the early period from hours to days. Because the system contains reactants of Na₂CrO₄ and FeCl₂, the most likely products would include Fe(III), Cr(III) and chloride compounds, and the situation is very complex. We made samples containing FeCl₂ alone, Cr(NO₃)₃ alone and the mixture of Na₂CrO₄ and FeCl₂ respectively, trying to compare the influence of different species like Cl⁻, Cr(III), Fe(II) and Fe(III) ions.

It is very clear that at 28 days, the total hydration degree of cement paste is decreased in all samples with an admixture of Cr(NO₃)₃ alone, FeCl₂ alone or the combination of Na₂CrO₄ and FeCl₂ at various concentration levels (Fig. 8-10 a, b and c). The larger the amount of an admixture, the smaller the degree of hydration in all samples. For the samples containing low concentrations of Cr(III) (0.1%), FeCl₂ (0.73%), and Cr(VI) (0.1%) + FeCl₂ (0.73%) respectively, the hydration degrees are almost the same being reduced from ~76% in pure OPC to 65% with the admixtures (Fig. 8-10a). On increasing the concentration of the additives by 10 fold, the retarding strength of Cr(III) (1.0%)
Fig. 8-10a. Comparison of OPC, OPC + Cr (0.1%) Samples cured at 28 days

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Fig. 8-10b. Comparison of OPC, OPC+ Cr (1.0%) Samples cured at 28 days

1. -- Total hydration degree
2. -- Percent silicate of $Q^1$
3. -- Percent silicate of $Q^2$
4. -- Percent silicate of $Q^3$
5. -- Percent silicate of $Q^4$
Fig. 8-10c. Comparison of OPC, OPC+ Cr (4.0%)
Samples cured at 28 days

1. -- Total hydration degree
2. -- Percent silicate of $Q^1$
3. -- Percent silicate of $Q^2$
4. -- Percent silicate of $Q^3$
5. -- Percent silicate of $Q^4$
remains almost the same as in the lower concentration sample; but the retarding effect of FeCl₂ or the mixture of Cr(VI) + FeCl₂ is observably stronger than that of the same species in low concentration, e.g. in the FeCl₂ (7.3%) sample the hydration degree drops to ~55% (Fig. 8-10b). When the amounts of admixture are increased by 40 fold, the retarding effects are much stronger. 4.0% Cr(III) decreases the hydration degree to ~50%, 29.2% FeCl₂ to ~45% and the mixture of the two makes hydration degree drop to only ~35% (Fig. 8-10c).

In OPC alone, dimeric silicate, Q¹, has become the dominant silicate species in hydrating cement at 28 days. This situation remains almost the same in the least-doped samples (Fig. 8-10a), except the least-doped FeCl₂ sample shows significant lower proportions of dimeric silicate. It appears that Cl⁻ has a stronger effect in decreasing the proportion of dimeric silicate than the corresponding amount of Cr(III) in all samples over the whole tested concentration range at 28 days, and at one year this stronger effect is even more obvious (Fig. 10 and Fig. 11). Those are the pieces of evidence that allow us to propose that Cl⁻ could decompose disilicate (Q¹) to monosilicate (Q⁰) at early stages of hydration and promote higher and more complex polymerization in the later period (discussed in Part 8-9 of this chapter).

Linear chain or simple ring silicate polymers (Q²) are decreased by Cr(III), FeCl₂ or the reacting system of Cr(VI) + FeCl₂ at all concentration levels tested at 28 days, but a significant amount of chain-branched polymers (Q³) are produced at the same time. Q³ is normally not observed in samples of hydrated OPC alone at 28 days of cure. The decrease of Q² units is largely due to the overall retardation of silicate hydration, and the observation of production of Q³ implies that the additives, individually or
simultaneously, promote higher and more complex polymerization in hydrating cement paste. The strength of effects of the additives seems similar, except in the highest portion sample (4.1% Cr + 29.2% FeCl₂) which leads to a dramatically lower amount of hydrated silicates (Fig. 8-10c).

The trend of a higher proportion of complex polymerization is much more obvious and dramatic in the one-year samples. The hydration of cement silicates approaches completion with the addition of 0.73% FeCl₂ or 0.73% FeCl₂ + 0.1% Cr(VI) respectively, and achieves more than 95% completion with 7.3% FeCl₂ or 7.3% FeCl₂ + 1.0% Cr(VI), compared to about 85% hydration in OPC alone. It is very impressive that 0.73% FeCl₂ or 0.73% FeCl₂ + 0.1% Cr(VI) changes the structure of the cement matrix so dramatically by decreasing the dominant component of dimeric silicates, Q¹, from more than 50% in one-year-old OPC alone sample to less than 10% (Fig. 8-11a). But 10 times more additive, 7.3% FeCl₂ or 7.3% FeCl₂ + 1.0% Cr(VI) respectively, does not make so much change, i.e. there is still ~25% dimers left in the doped samples (Fig. 8-11b).

There is about 100% increase in the proportion of linear chain or simple ring silicate polymers (Q²), i.e. increase from less than 30% to about 60%, with the addition of 0.73% FeCl₂ or 0.73% FeCl₂ + 0.1% Cr(VI) respectively at one year of cure, and Q² units become the dominant component in both the FeCl₂ and FeCl₂ + Cr(VI) samples. A small amount (~6%) of more complex silicate species (Q³) forms in OPC paste without additives in one year. The small amount (~6%) of Q³ is dramatically increased to ~40% by adding 0.73% FeCl₂ alone or 0.73% FeCl₂ + 0.1% Cr(VI) together (Fig. 8-11a).
It seems that the effects of admixtures are very similar between samples containing small amount of FeCl₂ alone and small amount of FeCl₂ + small amount of Cr(VI), but large amounts of the additives allow differences between their samples to be seen. In the sample with addition of 7.3% FeCl₂ alone, the proportion of internal Q² units remains almost the same (~30%) as in an OPC alone sample, but the proportion of the Q³ branching units is much higher (close to 50%) and becomes the dominant component. At the same time, in the sample with 7.3% FeCl₂ + 1.0% Cr(VI), the dominant component is still Q² internal units at about 50% and the Q³ branching units is the second most common component at ~30% (Fig. 8-11b). This may indicate the stronger effect of chloride anion alone in promoting more complex polymerization in cement hydration and also shows some influence of Cr(III) produced in this complex system.

One of our previous work[122] on the effects of nickel chloride and calcium chloride has also found the dramatic promotion of the production of Q² and Q³ units in samples of one year of cure, and the chloride appears to be the dominant species affecting the matrix.

8.11. Effects of FeSO₄

From the experimental data (Table 7-2a and Fig. 7-1, 7-2, 7-3), it is confirmed that FeSO₄ is also very effective in Cr waste treatment with cement, and it has been one of the reagents very commonly used for this purpose in industry [1, 2, 33]. But the data also point out that for samples cured for 1 year, the leaching concentrations of Cr are all much higher than that of the comparable samples at 28 days; the solid-state NMR analysis also shows profound influences on the cementitious matrix that is formed during the curing.
Fig. 8-11a. Comparison of OPC, OPC+ Cr (0.1%)
Samples cured at one year
Fig. 8-11b. Comparison of OPC, OPC + Cr (1.0%) Samples cured at one year

1. -- Total hydration degree
2. -- Percent silicate of Q^1.
3. -- Percent silicate of Q^2.
4. -- Percent silicate of Q^3.
5. -- Percent silicate of Q^4.
process of this S/S treatment system. This part of the chapter is focused on studying the effects of the SO$_4^{2-}$ salt added into the system.

Ranking as a weaker accelerator, SO$_4^{2-}$ is listed in Table 8-1. From the results of the present research work, however, FeSO$_4$ is a straightforward hydration retarder. FeSO$_4$ alone retards the hydration at all tested concentration levels and a higher proportion of FeSO$_4$ leads to more retardation of cement hydration. The amount of FeSO$_4$ required for reducing 4.0% (wt) Cr(VI) is about 35.2% (wt) in the sample, and when this amount of FeSO$_4$ is added alone to OPC the hydration is retarded to as low as 24%. It seems unusual, however, that the mixture of Cr(VI) + FeSO$_4$ does not retard at all at the 4.0% level of Cr(VI), and the reason is not clear (Fig. 8-11 and Table 8-6). Of course, the combined Cr(VI) + Fe(II) produces Fe(III).

AFm is often called low-sulfate calcium sulfoaluminate; AFt is high-sulfate calcium sulfoaluminate. The AFt (Al$_2$O$_3$ - Fe$_2$O$_3$ - tri) phases:

$$[\text{Ca}_3(\text{Al, Fe})(\text{OH})_6\cdot 12\text{H}_2\text{O}]_2\cdot x_3\cdot x\text{H}_2\text{O}, \quad x \leq 2.$$  

X can be one doubly charged anion or two singly charged anions. The 't' refers to the three units of CaX in an alternative formula, Ca$_3$(Al, Fe)-3CaX-yH$_2$O. The conditions for forming AFt are broadly similar to those for AFm, but at higher ratios of CaX to C$_3$(A,F). The most important phase of AFt is ettringite, [Ca$_3$Al(OH)$_6$·12H$_2$O]$_2$·(SO$_4$)$_3$·2H$_2$O or C$_3$A·3CS·H$_3$2; formed during the early hydration of most Portland cements$^{50}$. 

This early hydration in the presence of CaSO$_4$ (CS) occurs in two stages, both are strongly exothermic. The first stage is during the first 30 min, and yields ettringite; the
Fig. 8-12. $^{29}\text{Si MAS NMR Spectra}$
for 28 d cured OPC samples containing FeSO$_4$ alone (left) and Cr(VI) + 3FeSO$_4$ (right)
(a). 0.1% Cr; (b). 1.0% Cr; (c). 4.0% Cr.

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Table 8-6. $^{29}$Si MAS NMR Chemical Shifts (ppm) and Relative Area (% in Parentheses)
For 28 d cured OPC samples containing FeSO$_4$ alone and Cr$^{+6}$ + FeSO$_4$.
% — [Metal cation mass /cement mass ] x 100
Molar ratios of Fe(II) : Cr(VI) = 3:1

<table>
<thead>
<tr>
<th>Cr(%)</th>
<th>Fe(II)(%)</th>
<th>Q$^0$</th>
<th>Q$^1$</th>
<th>Q$^2$</th>
<th>Q$^3$</th>
<th>Q$^4$</th>
<th>Hydr.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0</td>
<td>-70.9 (26.9)</td>
<td>-78.5 (48.9)</td>
<td>-83.8 (24.2)</td>
<td>--</td>
<td>--</td>
<td>73.1</td>
</tr>
<tr>
<td>0.0</td>
<td>0.88</td>
<td>-71.0 (31.8)</td>
<td>-78.7 (48.5)</td>
<td>-83.7 (16.9)</td>
<td>-90.2 (2.8)</td>
<td>--</td>
<td>68.2</td>
</tr>
<tr>
<td>0.0</td>
<td>8.88</td>
<td>-71.0 (45.1)</td>
<td>-78.5 (40.2)</td>
<td>-84.3 (10.2)</td>
<td>-90.4 (4.5)</td>
<td>--</td>
<td>44.9</td>
</tr>
<tr>
<td>0.0</td>
<td>35.2</td>
<td>-71.1 (75.6)</td>
<td>-78.5 (16.9)</td>
<td>-84.3 (7.5)</td>
<td>--</td>
<td>--</td>
<td>24.4</td>
</tr>
<tr>
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<td>0.88</td>
<td>-71.0 (38.7)</td>
<td>-78.7 (43.8)</td>
<td>-84.2 (15.0)</td>
<td>-90.4 (2.5)</td>
<td>--</td>
<td>61.3</td>
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<td>-71.0 (57.8)</td>
<td>-78.5 (33.1)</td>
<td>-84.3 (5.3)</td>
<td>-90.4 (3.8)</td>
<td>--</td>
<td>42.2</td>
</tr>
<tr>
<td>4.0</td>
<td>35.2</td>
<td>-71.1 (27.1)</td>
<td>-78.9 (20.9)</td>
<td>-84.9 (44.2)</td>
<td>-90.5 (7.8)</td>
<td>--</td>
<td>73.9</td>
</tr>
</tbody>
</table>
second occurs at 24-48h, the ettringite reacts further and AFm are formed. The reactions may be:

\[
\begin{align*}
C_3A + 3C_SH_2 + 26H_2O & \longrightarrow C_6AS_3H_{32} \\
C_3A + C_6AS_3H_{32} + 4H_2O & \longrightarrow 3C_4AS_3H_{12} \\
C_3A + CH + 12H_2O & \longrightarrow C_4AH_{13}
\end{align*}
\]

(8-11-1) (8-11-2) (8-11-3)

If the system contains too little gypsum, or none, cements undergo 'flash' or 'quick' set, with much evolution of heat; plasticity is not regained on continued mixing, and the subsequent development of strength is poor. Flash set increases early reaction of the aluminate and ferrite, with the formation of plates of AFm, 5-10 µm in size, throughout the paste. The meshwork of plates accounts for the rapid stiffening; and for the subsequent poor strength development, possible explanations include the protective layers around the grains, and the large plates of AFm weakening microstructure [50].

Too much sulfate causes attack of OPC concrete that can lead to strength loss, expansion, cracking and disintegration. XRD shows that the attack leads to formation of ettringite and often also of gypsum [105]. The OH⁻ and Ca²⁺ required by these reactions are obtained by the dissolution of CH and decomposition of the hydrated silicate and aluminate phases. The expansion has generally been attributed mainly to the formation of ettringite and gypsum. The both can form in pore solution and, in the regions attacked the following reactions occur:

\[
6Ca^{2+} + 2Al(OH)_4^- + 4OH^- + 3SO_4^{2-} + 26H_2O \longrightarrow C_6AS_3H_{32}
\]

(8-11-4)
\[ \text{Ca}^{2+} + \text{SO}_4^{2-} + 2\text{H}_2\text{O} \rightarrow \text{CSH}_2 \quad (8-11-5) \]

The Al(OH)$_4^-$, OH$^-$ and some Ca$^{2+}$ could be supplied by unreacted aluminate or ferrite phases, but the main source of Al(OH)$_4^-$ in a hardened paste is likely to be AFm phase:

\[ \text{C}_4\text{ASH}_{12} \rightarrow 4\text{Ca}^{2+} + 2\text{Al(OH)}_4^- + 4\text{OH}^- + \text{SO}_4^{2-} + 6\text{H}_2\text{O} \quad (8-11-6) \]

Whichever provides the Al(OH)$_4^-$, and OH$, additional Ca$^{2+}$ is needed to form either ettringite or gypsum. In order to get the additional Ca$^{2+}$, CH dissolves and C-S-H is decalcified, initially by lowering its Ca/Si ratio, and ultimately by conversion into a highly porous, hydrous form of silica:

\[ \text{Ca(OH)}_2 \rightarrow \text{Ca}^{2+} + 2\text{OH}^- \quad (8-11-7) \]
\[ x\text{CaO} \cdot \text{SiO}_2(\text{aq}) + z\text{H}_2\text{O} \rightarrow y\text{Ca}^{2+} + 2y\text{H}_2\text{O} + (x-y)\text{CaO} \cdot \text{SiO}_2(\text{aq}) \quad (8-11-8) \]

The effect of the drying shrinkage of OPC with additional sulfate also suggests that the microstructure is modified by changes in the micromorphology of the C-S-H or by incipient precipitation of ettringite throughout the gel. The latter effect, if it happened at an early age or to a limited extent, could augment strength through a decrease in porosity, but if it happened later or to too large an extent, could decrease strength through localized expansions\textsuperscript{[30]}.
For most of the long-term (one year) samples containing FeSO₄, the hydration degrees are significantly higher than those of 28 day samples (Table 8-6 and 8-7). But the leachate concentrations of Cr from long-term samples are all much higher than those of the comparable samples at 28 days (Table 7-2). The sulfate attack could result in the following effects:

1). The consumption of CH to form ettringite or gypsum decreases pH of the system, thereby increasing the solubility of Cr(III) precipitates. Table 7-2a shows that the pH values drop with time and with additional amount of FeSO₄.

2). Cement strength depends principally on the clinker hydration forming C-S-H gel, but cements with a high degree of hydration do not necessarily retain high strength. Strength loss by sulfate-induced decalcification of C-S-H gel during the later period of curing could also explain the higher leachability of long-term samples.

This study has found another phenomenon: silicate depolymerization with increasing amount of iron sulfate and Cr compound in samples cured for one year (Table 8-7 and Fig. 8-12):

a). The sample containing no Cr and only 0.88% FeSO₄, finished complete hydration at 1 year. It shows a very high degree silicate polymerization: more than 95% signals of chain-linking (Q²) and chain-branching (Q³) groups. Adding 0.1% Cr, the result is basically similar with only a few percent less hydration and polymerization.

b). When FeSO₄ is increased to 8.80%, the higher polymers (Q² and Q³) drop to about 40%; and the sample begin to show significantly retarded hydration.
Table 8-7. $^{29}$Si MAS NMR Chemical Shifts (ppm) and Relative Area (% in Parentheses)
For 1 year cured OPC samples containing FeSO$_4$ alone and Cr$^{VI}$ + FeSO$_4$:

$\% = \frac{\text{Metal cation mass/cement mass}}{} \times 100$;

Molar ratios of Fe(II) : Cr(VI) were 3:1 and 6:1

<table>
<thead>
<tr>
<th>Cr(%)</th>
<th>FeSO$_4$(%)</th>
<th>Q$^0$</th>
<th>Q$^1$</th>
<th>Q$^2$</th>
<th>Q$^3$</th>
<th>Q$^4$</th>
<th>Hydr.%</th>
<th>Q$^d$</th>
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<td>0.00</td>
<td>0.88</td>
<td>--</td>
<td>-79.7 (2.7)</td>
<td>-84.7 (44.6)</td>
<td>-90.5 (52.7)</td>
<td>--</td>
<td>100.0</td>
<td>2.7</td>
</tr>
<tr>
<td>0.10</td>
<td>0.88</td>
<td>-71.1 (2.5)</td>
<td>-79.0 (11.3)</td>
<td>-84.5 (48.8)</td>
<td>-94.3 (37.4)</td>
<td>--</td>
<td>97.5</td>
<td>11.6</td>
</tr>
<tr>
<td>0.00</td>
<td>8.80</td>
<td>-71.1 (7.2)</td>
<td>-79.7 (39.7)</td>
<td>-84.7 (49.9)</td>
<td>-90.5 (3.2)</td>
<td>--</td>
<td>92.8</td>
<td>42.8</td>
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<td>-71.1 (19.2)</td>
<td>-79.6 (40.9)</td>
<td>-84.3 (39.9)</td>
<td>--</td>
<td>--</td>
<td>81.8</td>
<td>50.6</td>
</tr>
<tr>
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<td>2x8.80</td>
<td>-71.1 (24.4)</td>
<td>-78.9 (40.2)</td>
<td>-84.3 (35.4)</td>
<td>--</td>
<td>--</td>
<td>75.6</td>
<td>53.2</td>
</tr>
</tbody>
</table>

Q$^d$: the percentage of dimer and chain-ending SiO$_4^{4-}$ signal in the total signal of hydrated SiO$_4^{4-}$.
Fig. 8-13. $^{29}$Si MAS NMR Spectra for one year cured OPC samples
c). Samples containing double the stoichiometric ratio of Fe/Cr (2 x 0.88% and 2 x 8.80% of FeSO₄), does not show the higher polymerization (Q³). And the hydration process is retarded to almost the same degree as 28 day samples.

In summary, the addition of Fe(II) as a reducing agents for Cr(VI) is very effective to stabilize Cr ions in OPC. For a moderate amount of Cr and iron sulfate content, the S/S system can control the leaching concentration of Cr waste under the EPA drinking water limit.

But almost all chemicals added, including Cr species, influence the hydration process and the resulting cement matrix of the samples. The Cr(VI) + FeSO₄ system retards in this experimental series. FeSO₄ samples without Cr(VI) show impressive retardation effects as well. When FeSO₄ and Cr(VI) are mixed together, Cr(III) is produced and the retardation can be caused by the formation of protective layers of AFm phases and the precipitation of \((\text{Cr}_x\text{Fe}_{1-x})(\text{OH})_3\) species. The Cr(VI) samples are unlikely to form this kind of protective layers, and this could be an important reason for having less retardation and much higher leachability.

The system, especially for long-term samples, is subject to sulfate attack. The subsequent strength loss and pH decrease of the treatment system are probably responsibly for the observed higher leachability of Cr after one year of cure. The decalcification and the depolymerization of the C-S-H gel are adverse effects on the cement matrix, and they may explain why some samples with a high degree of hydration could have low strength and high leachability.
CHAPTER 9
RESULTS AND DISCUSSION OF EXAFS DATA

As mentioned in the background discussion, the two important oxidation states of Cr in natural waters are III and VI. Laboratory studies have indicated that Cr(III) and Cr(VI) are interconvertible under mild conditions. Cr(VI) can be easily reduced by Fe²⁺, H₂S, dissolved sulfides, and certain organic acids. The concentration of chromium in natural waters is limited by Cr(III) species due to their low solubility. The solid phases that are most likely to control Cr concentrations in natural environments are Cr(III) oxides, Cr(OH)₃, and Cr(III) coprecipitated with Fe oxides.

We have designed our EXAFS analysis program systematically to study Cr species and products. Cr(OH)₃ and the coprecipitation product of Cr(OH)₃ and Fe(OH)₃ were synthesized as reference substances. Reagent grade Cr₂O₃, CrO₃, Cr(NO₃)₃, and Na₂CrO₄ were subjected to EXAFS analysis with or without Fe(II) compounds and both within and without an OPC matrix.

The EXAFS results include structural information such as coordination number (N), interatomic distances (r), Debye-Waller factors (σ², the degree of vibrational and static disorder), and the types of neighbor atoms. In general, the resulting r values for the first coordination shell were accurate to ± 0.03 Å and N to ± 20% based on fits to model compounds, and more distant shells will be successively less accurate in both r and N.

9.1. FEFF Program

FEFF program version 7 was used to do EXAFS data calculation and simulation analysis in this work. FEFF is an automated program for ab initio multiple...
scattering calculations of EXAFS and XANES spectra for clusters of atoms. The code yields scattering amplitudes and phases used in many modern XAS analysis codes.

FEFF7 calculates wave phase shifts, effective scattering amplitudes and single and multiple scattering curved EXAFS and XANES spectra, including polarization dependence, for clusters of atoms (Z < 96) [144].

The calculation is automated and done sequentially in four steps [144, 145]:

9.1.1). The scattering potentials, phase shifts, dipole matrix elements and absolute energies are calculated.

The potentials of each atomic type are calculated as if the atoms were isolated in space using a relativistic Dirac-Fock Desclaux atom code. The scattering potentials are calculated by overlapping the free atom densities within the muffin tin approximation (Mattheiss prescription), and including the Hedin-Lundqvist/Quinn self energy for excited states. Muffin-tin radii are determined automatically from calculated Norman radii and scattering phase shifts are determined by matching at the muffin tin radius. EXAFS spectra are referenced to the threshold Fermi Level, which is estimated by electron gas theory at the mean interstitial density. Atomic configurations and core-hole lifetimes are built in, and mean free paths are determined from the imaginary part of the average interstitial potential. Dipole matrix elements are calculated using atomic core and normalized continuum wave functions. An absolute energy scale is obtained by a Desclaux-atom calculation of the total energy of the system with and without the core-hole.
9.1.2). The scattering paths for the cluster are enumerated.

Path enumeration uses a constructive algorithm with several path importance filters to explore all significant multiple-scattering paths in order of increasing path length, based on a list of atomic coordinates. An efficient degeneracy checker is used to identify equivalent paths (based on similar geometry, path reversal symmetry, and space inversion symmetry). The criteria used in filtering are based on increasingly accurate estimates of each path’s amplitude. The earliest filters, the pathfinder heap and keep filters, are applied as the paths are being created. A plane wave filter based on the plane wave approximation (plus a curved wave correction from multiple-scattering paths) and accurate to about 30% is applied after the paths have been enumerated and sorted. Finally, an accurate curved wave filter is applied to all remaining paths.

9.1.3). The effective scattering amplitudes and other EXAFS parameters are calculated for each scattering path.

9.1.4). The EXAFS parameters from one or more paths are combined to calculate a total EXAFS spectrum (curve-fitting).

EXAFS spectrum calculation constructs the EXAFS spectrum $x(k)$ (see Chapter 4) using the EXAFS parameters from one or more paths. Single and Multiple scattering Debye-Waller factors are calculated using a correlated Debye model. Output from this module is the total EXAFS spectrum and the contribution to the EXAFS from each path individually. Numerous options for filtering, Debye-Waller factors, and other corrections are available at this point $^{[144,145]}$.

Finally, it should be mentioned that the method of curve-fitting has not been powerful enough to elucidate structural environment beyond 4 $\sigma$ from the center atom $^{[144,145]}$. 

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An example of application of this program was demonstrated in Chapter 4.

9.2 EXAFS Data for Cr₂O₃

Fig. 9-1a is the Pseudo Radial Distribution (PRDF) of the Cr₂O₃ standard compound without OPC after Fourier transformation of the extracted EXAFS spectrum. Fig. 9-1b shows curve fitting of the PRDF calculations with the program FEFF7 based on crystal structure data \(^{145}\). Fig. 9-2a is the PRDF of the sample containing 4% (wt.) Cr₂O₃ mixed with OPC and cured at least 28 days, and Fig. 9-2b shows curve fitting of the PRDF with the same theoretical calculations based on the same crystal structure data used for Fig. 9-1b.

The PRDF shown in Fig. 9-1 and 9-2 disclose that the local structure of Cr₂O₃ was not altered by the cement hydration reactions after Cr₂O₃ was mixed with OPC clinker and water. The detailed results of structural information are summarized in Table 9-1. All of the major structural parameters like coordination number \((N)\), interatomic distance \((r)\), and Debye-Waller factors \((\sigma^2)\) are almost identical before and after being mixed with OPC.

As discussed in Chapter 4, Cr(III) substitution into C-S-H was reported previously by Tashiro \(^{58, 69}\). They suggested that 10% or more of Cr₂O₃ could enter into solid solution of C-S-H with Cr\(^{3+}\) substituting for both Ca\(^{2+}\) and Si\(^{4+}\). Our EXAFS data analysis obviously does not support this suggestion, because no structural change was observed for Cr₂O₃.
### Table 9-1. Structural Information from EXAFS Analysis

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fit</th>
<th>Atomic pair</th>
<th>r (Å)</th>
<th>N</th>
<th>θ²</th>
<th>E₀ shift</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr₂O₃, 100%</td>
<td>Three-shell fit</td>
<td>Cr-O</td>
<td>1.983</td>
<td>6</td>
<td>0.00397</td>
<td>-0.102</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cr-Cr</td>
<td>2.311</td>
<td>3</td>
<td>0.01752</td>
<td>7.549</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cr-Cr</td>
<td>2.869</td>
<td>3</td>
<td>0.00256</td>
<td>-10.51</td>
</tr>
<tr>
<td>Cr₂O₃, 4% (wt.) in OPC.</td>
<td>Three-shell fit</td>
<td>Cr-O</td>
<td>1.991</td>
<td>6</td>
<td>0.00279</td>
<td>5.611</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cr-Cr</td>
<td>2.262</td>
<td>3</td>
<td>0.01434</td>
<td>7.016</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cr-Cr</td>
<td>2.889</td>
<td>3</td>
<td>0.00239</td>
<td>-4.062</td>
</tr>
<tr>
<td>Synthesized Cr(OH)₃, 100%</td>
<td>Three-shell fit</td>
<td>Cr-O</td>
<td>1.985</td>
<td>6</td>
<td>0.00758</td>
<td>-2.059</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cr-Cr</td>
<td>2.937</td>
<td>1</td>
<td>0.00214</td>
<td>-5.579</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cr-Cr</td>
<td>4.154</td>
<td>1</td>
<td>0.00300</td>
<td>0.361</td>
</tr>
<tr>
<td>Cr(OH)₃, (4% wt. Cr(NO)₃ in OPC.)</td>
<td>Three-shell fit</td>
<td>Cr-O</td>
<td>1.988</td>
<td>6</td>
<td>0.00372</td>
<td>-2.952</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cr-Cr</td>
<td>2.351</td>
<td>1</td>
<td>0.01198</td>
<td>-9.277</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cr-Ca</td>
<td>3.422</td>
<td>4</td>
<td>0.00304</td>
<td>1.818</td>
</tr>
<tr>
<td>Synthesized Cr₆Feₓ₋ₓ(OH)₃, 100%</td>
<td>Failure of data collection.</td>
<td>Cr-O</td>
<td>2.005</td>
<td>6</td>
<td>0.00685</td>
<td>1.021</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cr-Cr</td>
<td>3.023</td>
<td>1</td>
<td>0.00813</td>
<td>-8.015</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cr-Ca</td>
<td>4.044</td>
<td>1</td>
<td>0.00758</td>
<td>-3.428</td>
</tr>
<tr>
<td>Cr product, 4% (wt.) Cr(VI) + 3FeCl₂ in OPC.</td>
<td>Three-shell fit</td>
<td>Cr-O</td>
<td>1.990</td>
<td>6</td>
<td>0.00679</td>
<td>-0.968</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cr-Cr</td>
<td>3.074</td>
<td>1</td>
<td>0.00402</td>
<td>-0.451</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cr-Ca</td>
<td>3.779</td>
<td>1</td>
<td>0.00503</td>
<td>-14.83</td>
</tr>
</tbody>
</table>
Fig. 9-1. EXAFS of Cr$_2$O$_3$ Reference Compound
a) PRDF of Cr$_2$O$_3$ sample
b) PRDF of Cr$_2$O$_3$ sample and curve-fitting

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Fig. 9-2. EXAFS of 4% (wt.) of Cr$_2$O$_3$ in OPC
a) PRDF of Cr$_2$O$_3$ sample in cement
b) PRDF of Cr$_2$O$_3$ sample and curve-fitting
9.3 EXAFS Data of Cr(OH)$_3$ and Cr(NO$_3$)$_3$

OPC mixed with various amounts of Cr in the form of nitrates [Cr(NO$_3$)$_3$], to simulate industrial waste, was studied by electron microscopy (SEM and TEM/STEM) \cite{65}. The authors proposed that Cr(III) was chemically incorporated in all hydrated cement phases, and appeared to substitute for Si in C-S-H gel. The Cr was present in highest concentration in association with calcium salts, e.g. Ca(OH)$_2$ and Ca(NO$_3$)$_2$.

The low solubility of Cr(III) species was also mentioned in previous Chapters. The solid phases that are most likely to control Cr concentrations in surface environments are Cr(III) oxides, Cr(OH)$_3$ and Cr(III) coprecipitated with Fe oxides \cite{23}.

In our lab, we synthesized Cr(OH)$_3$ with Na$_2$CrO$_4$ and FeSO$_4$ as one of our references. Fig. 9-3a and Fig. 9-3b show the EXAFS PRDF of pure Cr(OH)$_3$ \cite{146} and its curve fitting, respectively. From the figures and data in Table 9-1, we observe distinct structural differences between Cr(OH)$_3$ and Cr$_2$O$_3$. Although the first shell of the local structure for the center Cr atom still consists of six O atoms at almost the same average interatomic distance of about 1.99 Å, the second and the third shell structure of Cr in Cr(OH)$_3$ are much extended than that in Cr$_2$O$_3$. The distances between the central Cr and surrounding Cr atoms are significantly longer and Cr coordination numbers for the center Cr are reduced from ~3 to ~1 in both the second and the third shells.

We also mixed OPC clinker with 4% (wt.) of Cr in the form of nitrates [Cr(NO$_3$)$_3$] to simulate industrial waste. Due to the strong alkaline environment in OPC, it seems reasonable to assume that dissolvable Cr(NO$_3$)$_3$ will become product mainly in the form of Cr hydroxide during the process of hydration of OPC.
The EXAFS analyses reveal a complex situation. Fig. 9-4a, 4b and data in Table 9-1 describe the structural picture of the product (or products) of Cr(NO₃)₃ in OPC. There is little change for the first shell structure in terms of six coordinating oxygens at an average distance of 1.99 Å. However, the average interatomic distance of the second shell of Cr-Cr (2.35 Å) is much shorter than that (2.94 Å) in the structure of the pure Cr(OH)₃, and is longer than that (2.26 Å) in 4% Cr₂O₃ mixed with OPC. At a farther distance (3.42 Å) from the center Cr, coordinating Ca atoms appear to be indicated by curve-fitting analysis.

9.4 EXAFS Data of Products of Cr(VI) + FeCl₂ and Cr(VI) + FeSO₄ in OPC

To simulate treatment of industrial Cr waste, we mixed Na₂CrO₄ with FeSO₄ and FeCl₂ as reductants in OPC cement clinker. Fig. 9-5a, 5b and Fig. 9-6a, 6b show the EXAFS PRDF for the samples with an age of about one month hydration.

The EXAFS results show clear similarity for the Cr products in the FeCl₂ and FeSO₄ samples. The first shell of local structure of Cr consists of six oxygens at about 2.0 Å. The second shell is seen as one Cr atom contacting at 3.0 Å. One Ca atom is positive at a farther distance of about 3.8 to 4.0 Å.

The data in Table 9-1 and the PRDF from the EXAFS spectra show a considerable distinction from the structure of Cr₂O₃. They also differentiate themselves from pure Cr(OH)₃, though their structures are closer to the latter.

It was discussed earlier that one of the possible products of Cr would be coprecipitation of chromium hydroxide and iron hydroxide due to the very low solubility of the coprecipitates. We synthesized the hydroxide coprecipitate compounds with 3:1.
Fig. 9-3. EXAFS of Cr(OH)$_3$ Reference Compound
a) PRDF of Cr(OH)$_3$ sample
b) PRDF of Cr(OH)$_3$ sample and curve-fitting
Fig. 9-4. EXAFS of 4% (wt.) of Cr(NO$_3$)$_3$ in OPC
a) PRDF of Cr(NO$_3$)$_3$ sample in cement
b) PRDF of Cr(NO$_3$)$_3$ sample and curve-fitting
Fig. 9-5. EXAFS of 4% (wt.) of Cr(VI) + FeCl₂ in OPC
   a) PRDF of Cr(VI) + FeCl₂ sample in cement
   b) PRDF of Cr(VI) + FeCl₂ sample and curve-fitting

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Fig. 9-6. EXAFS of 4% (wt.) of Cr(VI) + FeSO₄ in OPC
a) PRDF of Cr(VI) + FeSO₄ sample in cement
b) PRDF of Cr(VI) + FeSO₄ sample and curve-fitting
Table 9-2. Comparison of Curve-fittings for EXAFS Data of Cr(VI) + FeSO₄ sample in OPC

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fit</th>
<th>Atomic pair</th>
<th>r (Å)</th>
<th>N</th>
<th>χ²</th>
<th>E₀ shift</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr product, 4%(wt.) Cr(VI) + 3FeSO₄ in OPC.</td>
<td>Three-shell fit</td>
<td>Cr-O</td>
<td>1.990</td>
<td>6</td>
<td>0.00679</td>
<td>-0.968</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cr-Cr</td>
<td>3.074</td>
<td>1</td>
<td>0.00402</td>
<td>-0.451</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cr-Ca</td>
<td>3.779</td>
<td>1</td>
<td>0.00503</td>
<td>-14.83</td>
</tr>
<tr>
<td>Cr product, 4%(wt.) Cr(VI) + 3FeSO₄ in OPC.</td>
<td>Three-shell fit</td>
<td>Cr-O</td>
<td>1.985</td>
<td>4</td>
<td>0.00207</td>
<td>-1.307</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cr-Cr</td>
<td>3.145</td>
<td>1</td>
<td>0.00424</td>
<td>-5.474</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cr-Ca</td>
<td>3.783</td>
<td>1</td>
<td>0.00148</td>
<td>12.36</td>
</tr>
<tr>
<td>Cr product, 4%(wt.) Cr(VI) + 3FeSO₄ in OPC.</td>
<td>Three-shell fit</td>
<td>Cr-O</td>
<td>1.985</td>
<td>4</td>
<td>0.00218</td>
<td>-1.219</td>
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<tr>
<td></td>
<td></td>
<td>Cr-Cr</td>
<td>3.145</td>
<td>2</td>
<td>0.00881</td>
<td>4.898</td>
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<td></td>
<td></td>
<td>Cr-Ca</td>
<td>3.806</td>
<td>1</td>
<td>0.00571</td>
<td>-12.56</td>
</tr>
</tbody>
</table>

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Fig. 9-7. Curve-fitting (2) of Cr(VI) + FeSO₄ in OPC
a). PRDF of Cr(VI) + FeSO₄ sample in cement
b). Four O curve-fitting
Fig. 9-8. Curve-fitting (3) of Cr(VI) + FeSO₄ in OPC
a). PRDF of Cr(VI) + FeSO₄ sample in cement
b). Four O and two Cr curve-fitting
ratio of Cr:Fe as another reference substance. But, unfortunately, experimental
difficulties prevented collecting EXAFS data for this sample. This part of the work will
be continued in near future.

Fig. 9-7 and Fig. 9-8 present curve-fittings with different structural parameter
control for the sample of 4% Cr(VI) + FeSO₄ mixed in OPC. Compared to the fitting in
Fig. 9-6 for the same sample, the fittings in Fig. 9-7 and Fig. 9-8 are acceptably good
and not physically impossible in terms of Debye-Waller factor ($\sigma^2$) (Table 9-2).

The fittings in Fig. 9-7 and 9-8 result in some major differences in structural
parameters. One of those is the coordination number of Cr in the first shell, which is
fitted with 4 oxygen atoms. If this is the case, it can be supportive evidence for the
substitution theory [50, 65], which suggested that Cr might substitute for Si in the silicate
ions ($\text{SiO}_4^{2-}$) in the C-S-H structure of the cement paste through the formation of $\text{CrO}_4^{3-}$.
The charge imbalance might be offset by other ions like H⁺ or $\text{H}_3\text{O}^+$.

At this stage, it still remains a question which fitting, six O or four O, is closer to
reality. Considering the high degree complexity in cement matrix, a mixture of both or a
structure that is distorted in some manner might be more realistic. Another question is
how many Cr atoms are present in the second shell. The curve-fittings in figure 9-7 and
9-8 produce data summarized in Table 9-2. The results are one or two surrounding Cr
atoms at about 3.14 Å. This may be the best answer for the real-world situation in OPC
cement.
CHAPTER 10
CONCLUSIONS AND RECOMMENDATIONS

The conclusions reached in the present studies and recommendations for further research based on the information gained in the work are summarized in this chapter.

10.1. Conclusions

1. Poor performance of all of the tested binders and additives toward immobilization of Cr(VI) was observed. By contrast, Cr(III) was readily immobilized.

Reduction of Cr(VI) to Cr(III) has been applied in the waste treatment processes. Fe(II) compounds are the commonly used reducing reagents reported in the literature and this study has confirmed their effectiveness. The reduction not only removes the toxic Cr(VI) species but also results in the precipitation of \((\text{Cr}_x\text{Fe}_{1-x})(\text{OH})_{3+}\) in the solidification/stabilization (S/S) system. The solubility of this solid limits Cr(III) concentrations over a wide pH range.

S/S is an economical process for the disposal of many types of hazardous wastes. using binders like Type I Portland cement (ordinary Portland cement, OPC) or OPC plus fly ash and kiln dust materials. A high resulting pH in the pore waters for the cement-solidified waste is observed, which is considered valuable to precipitate heavy metals and limit their leaching.

It is found by the current research that combination of the two techniques; namely reduction of Cr(VI) to Cr(III) and simultaneous immobilization within a cement matrix, is effective and practical to treat Cr wastes. The effects of Fe(II) salts are dramatic. For the samples containing 100,000 ppm of Cr(VI) originally, the addition of
FeSO$_4$ reduces the leachability of Cr(VI) by more than 100 fold at age 28 days; and FeCl$_2$ by more than 10 fold at 28 days. At the 10,000 ppm and the 1,000 ppm Cr(VI) level, all three iron reagents, namely FeSO$_4$, FeCl$_2$ and Fe$_3$O$_4$ are able to control Cr leaching concentration below the releasing limit of 5 ppm at 28 days. FeCl$_2$ appears the most effective at 28 days and 1 year of cure.

Over-dose (6:1 Fe:Cr) of Fe(II) as reducing reagent gives encouraging results. The iron salts in higher than stoichiometric proportions can decrease the leaching concentrations of most Cr(VI) containing samples by one or two orders of magnitude. And there are no extra retardation effects on the cement hydration compared to most of the 3:1 ratio samples.

Fe$_3$O$_4$ was included in these studies as a cheap source of iron. But it is not as efficient as a pure Fe(II) salt. The use of Fe$_3$O$_4$ in any of these system does not appear practical.

The long-term stability of this reducing-fixing S/S treatment is a concern. The leachate concentrations of Cr are more than doubled from age 28 days to one year for almost all samples of the three Fe additives. Nevertheless, there is still a low level of leachability that would be protective of the environment.

2. Many metal ions have a profound influence on the cementitious matrix formed during the curing process of Portland cement. Both Cr(III) and Cr(VI) species are set retarders, and FeSO$_4$ and FeCl$_2$ look like retarders too.

All samples containing Cr(III) in various concentrations show a reduced hydration degree after 28 days of cure. For the samples containing 0.1% and 1% of Cr(III), the reduction effects are similar, the total hydrated silicates percentage is
decreased from about 70±5% to about 60±5%. When Cr(III) is as high as 4%, the hydration decline is more obvious, and the hydration degree reaches only 50%.

At 28 days the dominant silicate species in hydrated OPC alone appears to be dimers. When Cr(III) is added, the corresponding $^{29}\text{Si}$ signals indicate that the Cr(III) leads to a greater degree of longer chain silicate polymerization. The Cr(III) samples also show a significant amount of chain branched $Q^3$ silicates, which is not observed in the pure OPC sample. Generally, the more Cr(III), the less $Q^1$ and $Q^2$ and the more $Q^3$.

Cr(VI) retards the hydration process too, but not as much as Cr(III) does at 28 days in terms of total hydration degree. 40,000 ppm Cr(VI) and Cr(III) reduce the degree of hydration of pure OPC from about 73% at 28 days to ~69% and ~50% respectively. The enhancement of polymerization of Cr(VI) (to produce more of the chain branched silicates, $Q^3$) is almost the same as with Cr(III).

Cr(VI) has much less retardation effect than Cr(III). The reason may relate to the higher solubility of Cr(VI) species. But, no acceleration effect of Cr(VI) is observed either, as has been suggested by others from calorimetric studies.

Because the chemistry for Cr(VI) and Cr(III) is quite different, the effects of Cr(VI) and Cr(III) respectively on a cement matrix are very different. The leachability, the long term stability, the process of hydration and the matrix structure of the cement samples are dependent on the Cr(VI) or Cr(III) species. Furthermore, the additions of reducing chemicals into the binding agent of OPC, which alone is very complex, make the situation even more complex.

Usually, there was no iron hydroxide gel formed in normal OPC hydrated pastes, since the Fe$^{3+}$ entered the AFm phase. AFm phases containing Fe$^{3+}$ are colorless. In our
studies, samples containing iron atoms added to above 12% (wt), show obvious brown colors. Hence, extra Fe\(^{3+}\) forms iron(III) oxide, or hydroxide, or (and) Fe and Cr coprecipitates. Formation of relatively large amount of these species produces protective precipitated layers over the cement grains, and could be one of the most important causes for the retardation.

3. Several mechanisms for early hydration of C\(_3\)S in the cement have been proposed in past decades. Generally, they can be divided into two categories:

   a). The osmotic model (or gel model, or protective coating model).

   b). The crystalline model (or delayed nucleation model).

From studies of thermal analysis, some researchers had assessed that Cr species were accelerators of cement hydration, because, with the osmotic model in mind, Cr(VI) calcium salt is soluble; and Cr(III) was detected mainly in the hydrated cement structure but not on the surface. But, our studies with the analysis of solid state NMR have obtained opposite results compared to the accelerator assessment of Cr species.

The "accelerator assessment" of Cr is based on the second heat evolution peak of the thermal analysis curve, largely corresponding to the early hydration reactions of the C\(_3\)S phase of the cement. The appearance of the C-S-H gel during this early stage is also found by the \(^{29}\)Si NMR and \(^1\)H relaxation time measurements.

The structure of the cement matrix is significantly modified by Cr, especially Cr(III), and we have observed strong retardation effects of the Cr and Fe salts in the hydrating cement paste. Therefore, we disagree with the common assessment that Cr(VI), Cr(III) and chloride can be expected to be accelerators in most, if not all, circumstances.
Cr(VI) has significant less retardation effect, hence less modification effects on the structure of cement matrix than Cr(III), but much higher leachability. It may imply that the mechanism for the S/S system with OPC to immobilize Cr wastes is likely a chemical one rather than something else dependent on physical strength of cement matrix.

In the crystalline model, the initial nucleation and growth of crystals of Ca(OH)₂ is very important. Regarding this model, the formation of the species like (CrₓFe₁₋ₓ)(OH)₃ and AFm phases, and Fe(OH)₃ in the samples with a high portion of admixtures, needs to consume large amount of hydroxyl. That causes competition for OH⁻ away Ca²⁺ during the induction period. The lower availability of OH⁻ should delay the nucleation of Ca(OH)₂ and extend the induction or dormant period.

4. The $^{29}$Si NMR is applied in the study of the S/S system with FeCl₂ and Cr(VI). Dramatical changes are observed in the hydration process from that seen for OPC alone. The degree of silicate hydration is decreased from the beginning, followed by rapid hydration after about 7 days. And at one year, the doped samples end up with higher proportions of hydrated silicates compared to OPC alone.

The admixture systems of Cr(VI) + FeCl₂ at 0.1 % and 1.0% levels produce a second dormant period during which the proportion of the hydrated silicates actually decreases during the period of from 8 hours to 7 days. After 7 days, an accelerating period shows up and the admixture samples achieve approximately 100% hydration at 1 year of cure, which is a higher degree of hydration than for OPC alone. All tested samples over the concentration range of 0.1% to 4% Cr and corresponding FeCl₂ in 3:1 system have a common low degree of hydration at the 7 days.
The samples of 6:1 (Fe:Cr) also retard the hydration process for the early period with the increased amount of FeCl₂. But, after a year of cure, the hydration degree is higher than the pure OPC samples and about the same as that in the 3:1 series samples.

It is clear that the addition of FeCl₂ and Cr salts (both 6:1 and 3:1) reduces the hydration degree of the OPC cement during the whole critical early hydrating period from hours to days. It is not clear, however, why the double amount (1.46%) of FeCl₂ showed the obviously stronger retarding effect at 8 hours compared to the stoichiometric amount (0.76%) of FeCl₂, but a smaller retarding effect at 1 day and 7 days. There is no significant difference between the 6:1 and 3:1 samples at 28 days and one year in the portion of the hydrated silicates.

In the 6:1 system, the samples of 1.0% Cr with 14.6% FeCl₂ have significantly stronger retarding effects than the samples of 0.1% Cr with 1.46% FeCl₂ from 8 hours to 28 days. This is another evidence that Cr species and FeCl₂ are retarders for OPC hydration. When the content of Cr is as high as 4%, with 58.4% FeCl₂ in 6:1 series, and 29.2% FeCl₂ in the 3:1 series, respectively, the retarding effects are very obvious during the entire early hydration period up to 28 days. The hydrated silicates remain around one fifth of the amount of hydrated silicates in the pure OPC samples for about the first 7 days. More FeCl₂ leads to stronger retardation in this system.

The hydration reversal is mainly at the cost of the dimer and chain-end silicates, Q¹, for the Cr-containing samples from 8 hours to 7 days. From 7 days, there is an accelerating formation of dimer or chain-ending silicates, and it peaks at 28 days. This phenomenon happens for all 3:1 samples. After 28 days the monosilicates continue to disappear and more dimer becomes higher degree polymers of silicates. There is no
obvious hydration reversal in the higher concentration (Fe:Cr = 6:1) samples during the early hydration. The reason is probably that the amount of unhydrated silicates, Q°, is still too high at 8 hours.

In short, based on the experimental data from $^{29}$Si NMR and the theoretical discussion of the cement chemistry above, we found more reasons for us to expect Cr(VI), Cr(III) and FeCl$_2$ to be retarders rather than accelerators in cement hydration.

5. The addition of the Cr(VI) + FeCl$_2$ retards the early cement hydration until 7 days, but it promotes the higher polymerization of silicates in the hydrating paste after 28 days and makes the silicate polymers (higher than dimer) become the dominant portion in long-term of cure.

Before the 7th day, much lower portion of middle and internal groups of silicates, Q$^2$, is observable in all 3:1 series samples. After 28 days, more and more higher polymers are produced with the decrease of the monosilicate and the disilicates. The Q$^2$ groups became the largest portion of the silicates at one year of cure, while the dimer, Q$^1$, is the largest in the OPC alone sample with the same age. The chain-branching group, Q$^3$, appears much earlier from 7 days of the hydration and becomes much higher proportion of ~30% to ~40% in one year, compared to ~6% of Q$^3$ in the OPC alone sample of one year of cure.

The 6:1 samples also end up with lower proportion of the disilicates at one year compared to the control. The retarding effects are stronger in the 6:1 samples than in the 3:1 samples for the 4.0% and the 1.0% Cr, respectively. The developments of the higher degree polymerization of hydrated silicates are similar in the 6:1 samples and in the 3:1...
samples. The growth of the middle and internal groups, \( Q^2 \), is accelerated after 28 days, and the \( Q^2 \) groups becomes the largest portion of the silicates in one year samples.

The distribution and the development of the chain-branching silicates, \( Q^3 \), are also similar for both the 6:1 and the 3:1 series. The formation of the higher polymers are enhanced by the addition of the mixture of Cr(VI) and FeCl\(_2\), and the proportion of the higher polysilicates are dramatically higher than that in the sample of the OPC alone.

6. No accelerating effects of chloride are observed in this study. The existence of a significant amount of chloride may play a role in the decomposition of the early hydration product of dimeric silicate (\( Si_2O_7^{6-}, Q^1 \)) back to monosilicate (\( SiO_4^{4-}, Q^0 \)) from 8 hours to 7 days, and in the higher degree of polymerization of \( Q^3 \) and \( Q^4 \) in later hydration. This is a subject remaining unclear.

It is clear that at 28 days, the total hydration degree of cement paste is decreased in all samples with an admixture of Cr(NO\(_3\)) alone, FeCl\(_2\) alone or the combination of Na\(_2\)CrO\(_4\) and FeCl\(_2\) at various concentration levels. The larger the amount of an admixture, the smaller the degree of hydration in all samples. The retarding strength of Cr(III) (1.0%) remains almost the same as in the lower concentration sample; but the retarding effect of FeCl\(_2\) or the mixture of Cr(VI) + FeCl\(_2\) is observably stronger than that of the same species in low concentration. 4.0% Cr(III) decreases the hydration degree to \(~50\%\), 29.2% FeCl\(_2\) to \(~45\%\) and the mixture of the two makes hydration degree drop to only \(~35\%\).

The least-doped FeCl\(_2\) sample shows significant lower proportions of dimeric silicate. It appears that Cl\(^-\) has a stronger effect in decreasing the proportion of dimeric silicate than the corresponding amount of Cr(III) in all samples over the whole tested
concentration range at 28 days, and at one year this stronger effect is even more obvious. Those are the pieces of evidence to propose that Cl$^-$ could decompose disilicate (Q$^1$) to monosilicate (Q$^0$) at early stages of hydration and promote higher and more complex polymerization in the later period.

7. FeSO$_4$ is also very effective in Cr waste treatment with cement. But for samples cured for 1 year, the leaching concentrations of Cr are all much higher than that of the comparable samples at 28 days.

The system, especially for long-term samples, is subject to sulfate attack. The subsequent strength loss and pH decrease of the treatment system are probably responsible for the observed higher leachability of Cr after one year of cure. The decalcification and the depolymerization of the C-S-H gel are adverse effects on the cement matrix, and they may explain why some samples with a high degree of hydration could have low strength and high leachability.

The sulfate attack could result in the following effects:

1). The consumption of CH to form ettringite or gypsum decreases pH of the system, thereby increasing the solubility of Cr(III) precipitates. Experimental data shows that the pH values drop with time and with additional amount of FeSO$_4$.

2). Cement strength depends principally on the clinker hydration forming C-S-H gel, but cements with a high degree of hydration do not necessarily retain high strength. Strength loss by sulfate-induced decalcification of C-S-H gel during the later period of curing could also explain the higher leachability of long-term samples.
The solid-state NMR analysis shows profound influences on the cementitious matrix that is formed during the curing process of this S/S treatment system. FeSO$_4$ retards the hydration at all tested concentration levels and a higher proportion of FeSO$_4$ leads to more retardation of cement hydration.

Another phenomenon is silicate depolymerization with increasing amount of iron sulfate and Cr compound in samples cured for one year. When FeSO$_4$ is increased to 8.80%, the higher polymers ($Q^2$ and $Q^3$) drop to about 40% compared to 95% of $Q^2$ and $Q^3$ in the 0.88% FeSO$_4$ sample; and the higher FeSO$_4$-content sample begins to show significantly retarded hydration. Samples containing 6:1 ratio of Fe/Cr does not show the higher polymerization ($Q^3$). And the hydration process is retarded to almost the same degree as 28-day samples.

8. X-ray absorption fine structure (XAS) was successfully applicable in speciation of Cr(III) and Cr(VI) in complex cement matrix. The pre-edge region of the Cr XANES spectra is characterized by pre-edge features, corresponding to the excitation of a core level (e.g. 1s) electron toward bond, or delocalized, empty states. A measurable shift in the XANES spectra is correlated to the difference in oxidation states of the element. The ratio of Cr(VI) to total Cr in a cement-based S/S system was measured, and the effectiveness of different Fe(II) reductants is determined from XANES and compared to leachability results.

EXAFS is a probe of the structural distribution in the immediate vicinity (about less than 5 Å) of the absorbing atom. Besides interatomic distances, EXAFS contains other structural information such as coordination number, Debye-Waller factors (the degree of vibrational and static disorder), and the types of neighbor atoms. FEFF
program was employed to analyze EXAFS data and to do curve fitting – calculating and simulating structural information of the experimental samples.

The EXAFS analysis disclosed that the local structure of Cr$_2$O$_3$ was not altered by the cement hydration reactions after Cr$_2$O$_3$ was mixed with OPC clinker and water. This observation does not support the suggestion that Cr$_2$O$_3$ could enter into solid solution of C-S-H with Cr$^{+3}$ substituting for both Ca$^{2+}$ and Si$^{4+}$. Distinct structural differences between Cr(OH)$_3$ and Cr$_2$O$_3$ were also observed. EXAFS analyses reveal a complex situation in the structural picture of the product (or products) of Cr(NO$_3$)$_3$ in OPC. EXAFS results show clear similarity and difference for the Cr products in the FeCl$_2$ and FeSO$_4$ samples.

10.2. Recommendations

This program has gathered relatively complete and systematic data to prove that almost all of the chemical species involved in this Cr waste treatment system are retarders during the crucial early hydration period of cement and have profound influences on the hydrated cement matrix. This achievement corrects the consensus view of "accelerator assessment" of Cr species, which is based on the classic calorimetric studies. Some more detail research are recommended for future work.

1. Use solid state $^{53}$Cr NMR to monitor and study Cr species directly during the reaction and hydration process. The fast development of instruments of high-resolution solid state NMR make it very positively practical.

2. Electronic spin resonance spectroscopy (ESR) can be applied in studying the Cr(III) and Fe(III) hydroxides or their mixed phases or coprecipitates. Those are obviously important phases in this S/S system.
3. More studies for early hydration stages from hours to 7 or 14 days to observe the influence of single species, like Cr(III), Cr(VI), Fe(II), Fe(III), Cl\(^{-}\), SO\(_4^{2-}\) etc. This would help to understand the complex system better.

4. Conduct calorimetric experiments to compare heat evolution between the doped samples and OPC alone in early hydration.

5. Conduct calorimetric experiments to observe phase changes in order to study possible sulfate attack phenomenon in long-term samples.

6. Since leachate concentrations of Cr are more than doubled from age 28 days to one year old for almost all samples of the three Fe additives, XANES will be very useful in analysis of the speciation of Cr oxidation state compounds in cement matrix on this aging effect to study the chemical mechanism of leaching increase.

7. The ability of EXAFS analysis is still limited by its complex calculation and data manipulation. More studies of standard and reference compounds, better experimental conditions and higher resolution measurement are needed. Other cross-examinations with different methods are also necessary on such complex cement-base system.
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