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ORIGINAL CONTRIBUTION

THE INTERFACIAL CHEMISTRY OF SOLIDIFICATION/STABILIZATION OF METALS IN CEMENT AND POZZOLANIC MATERIAL SYSTEMS

M. Yousuf, A. Mollah,* Rajan K. Vempati, T.-C. Lin and David L. Cocke†

Gill Chair of Analytical Chemistry, Lamar University, Beaumont, TX 77710, U.S.A.

ABSTRACT. The chemistry of cement, its hydration and mechanisms of solidification/stabilization (s/s) of toxic metals by cement-based systems and pozzolanic materials are significantly controlled by surface, near-surface and interfacial phenomena. The adsorption conditions and the selectively strong affinity of hazardous metals towards clay minerals, certain hydrated metal oxides and oxyhydroxides, and cementitious substances also play an important role in the s/s process for the immobilization of contaminants. Recent works from our laboratory involving metal ions and superplasticizers have elucidated the mechanisms of reactions leading to the retardation of cement hydration and subsequent setting and their interactions with silicate-based systems. This article delineates the current status of interfacial chemistry at the solid-liquid boundary and places it in perspective with present and future s/s processes based on Portland cement and pozzolanic materials. The importance of surface charge, the role of interfacial phenomena on adsorption, and the importance of calcium and other types of anions and cations in s/s are also discussed. A surface charge control reaction model that accounts for the importance of calcium and other cations and anions is outlined and used to discuss the chemical nature and microstructure of the interfacial transition zone.

INTRODUCTION

The release of metal species into air, soil and water is becoming more significant with increasing industrialization and other anthropogenic activities. Metal pollutants may be derived from industrial wastes generated by manufacturing industries, extraction processes, chemical weathering of wastes, landfills, mining operations, atmospheric deposition of materials resulting from the burning of fossil fuels, smelting ores, etc. Many natural phenomena like water-rock interactions, biodegradation and atmospheric deposition from volcanic activities also contribute to the addition of metals into the environment. One growing concern has been the safe disposal of the

solid inorganic hazardous wastes generated by different industrial processes. It has now become a common practice in the U.S.A. to isolate these solid hazardous wastes from the environment by fixing into cement-based or pozzolan-based (fly ash, silica fume, cement kiln dust, etc.) solidification/stabilization (s/s) systems, where the waste is physically contained and/or chemically bound. A number of authors have reviewed the chemical treatments of wastewater for s/s of hazardous heavy metals.¹ These traditional waste treatment methods include chemical precipitation, coagulation, flotation, ion-exchange, oxidation/reduction, electrochemical extraction, adsorption and membrane separation. Various aspects of chemical treatment of aqueous wastes and sludge have also been reviewed by other researchers.^{2,3} In this study the interfacial phenomena controlling the s/s of toxic metal species using cement and pozzolan-based systems and the mechanisms of such processes are discussed.

Solidification/Stabilization

Stabilization is a process of converting a toxic waste to a physically and chemically more stable form. It involves chemical interactions between waste and the

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*Visiting Professor, Department of Chemistry, University of Dhaka, Dhaka-1000, Bangladesh.

†To whom correspondence may be addressed.

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binding agent. Fixation, as defined by Tittlebaum *et al.*,⁴ also refers to the stabilization process. Solidification is the process of converting a liquid or a semi-solid sludge waste into a monolithic solid form or granular solid material that will allow easy handling and transportation to landfill sites. This does not necessarily involve chemical interactions between waste and the binding agent. The solidification is achieved by: (a) chemical means (e.g. formation of precipitates, reactions with cement, etc.); (b) isolation in a protective binding agent (e.g. imbedding in polymers, thermoplastic materials, etc.); and (c) physical means (e.g. evaporation of water from aqueous wastes or sludge, sorption onto an appropriate solid adsorbent, vitrification, etc.). Together, the solidification and stabilization processes are popularly known as solidification/stabilization (s/s). The combined effect of s/s is to prevent pollutants from migrating into the environment by making the toxic contaminants physically immobile and/or chemical bonding to the binders. The containment of the waste by s/s is expected to improve its handling characteristics and lower the leaching rate by reducing the surface area of the solid. Several review articles⁵⁻⁹ summarize the s/s technology. The most recent articles^{10,11} have addressed the chemical aspects involved in s/s processes. The fundamental physico-chemical processes controlling the s/s of these hazardous substances and the complexity of the problems involved have been reported elsewhere.¹² Some of these processes are schematically illustrated in Fig. 1.

This figure demonstrates the complexity of the problem by sketching several types of interactions that may occur simultaneously (and in some cases sequentially) in the solidified systems. The waste component may react in one or more of the following ways: adsorption, chemisorption, precipitation, ion-exchange, passivation, surface complexation, inclusions (micro encapsulation) and chemical incorporation into the hydrated cement system. Other phenomena, known as diadochy and isomorphic substitution, may also take place under appropriate conditions. In the former case an element is substituted for another of similar size and charge in a

crystal lattice;¹³ whereas in the latter case ions of similar sizes but with different charges may substitute in the crystal structure. Solidification processes used for waste disposal include: cement-based techniques; lime-based techniques; lime-pozzolan systems; thermoplastic techniques (bitumen, paraffin, and polyethylene ethylene); organic polymers and vitrification. Combinations of Portland cement, cement kiln dust, soluble silicates, fly ash, agricultural wastes, ground blast furnace slag, lime and other additives are mixed with wastes to: (a) increase the bearing strength, (b) eliminate free liquids, and (c) reduce leachability before landfilling. The chemical compositions of these materials include large amounts of calcium, silicon, or both, that have been converted into their respective oxides during high-temperature oxidation processes.¹³

Cement Chemistry

Portland cement is a heterogeneous mixture of four main compounds with the following composition: (i) 50–70% of tricalcium silicate (Ca_3SiO_5), (ii) 20–30% of dicalcium silicate (Ca_2SiO_4), (iii) 5–12% of tricalcium aluminate ($\text{Ca}_3\text{Al}_2\text{O}_6$), and (iv) 5–12% of calcium aluminoferrite ($\text{Ca}_4\text{Al}_2\text{Fe}_2\text{O}_{10}$). In cement chemistry these components are abbreviated as: C_3S (alite) for tricalcium silicate; $\beta\text{-C}_2\text{S}$ (belite) for dicalcium silicate; C_3A for tricalcium aluminate and C_4AF for calcium aluminoferrite. Additional components such as gypsum are sometimes added (ca. 2–5%) to delay the initial setting time by about 1–2 h to ensure a period of plasticity. The hydration of dry clinker leads to the formation of mainly: (i) 20–25% of $\text{Ca}(\text{OH})_2$ (portlandite, CH), (ii) 60–70% of $3\text{CaO} \cdot 2\text{SiO}_2 \cdot 3\text{H}_2\text{O}$ (calcium-silicate-hydrate, C-S-H), and (iii) 5–15% of other solid phases.¹⁴ The principal hydration product, C-S-H, has a variable composition and its morphology is dependent on the Ca/Si ratio, setting conditions and water/solid ratio. The hydration and subsequent setting of cement paste progresses through a series of competing chemical reactions.¹⁰ These reactions are exothermic and the negative enthalpies of cement hydration greatly influence: (a) hydration rate, (b) microstructure and (c) morphology of the hardened concrete. The mechanisms of these reactions are quite complex and not yet fully understood. However, two models: (i) the gel or osmotic model and (ii) the crystalline model, have been proposed to explain the observed phenomena associated with cement hydration and subsequent setting.¹⁵

The Gel Model

According to this model, a membrane of C-S-H gel is formed on the cement particle's surface upon hydration (Fig. 2). This membrane formed around the cement grains permits the inward flow of water

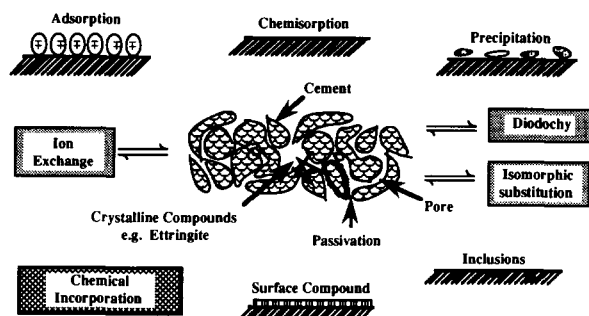


FIGURE 1. Possible interactions of hazardous substances with cement particles (adapted from Ref. 12).

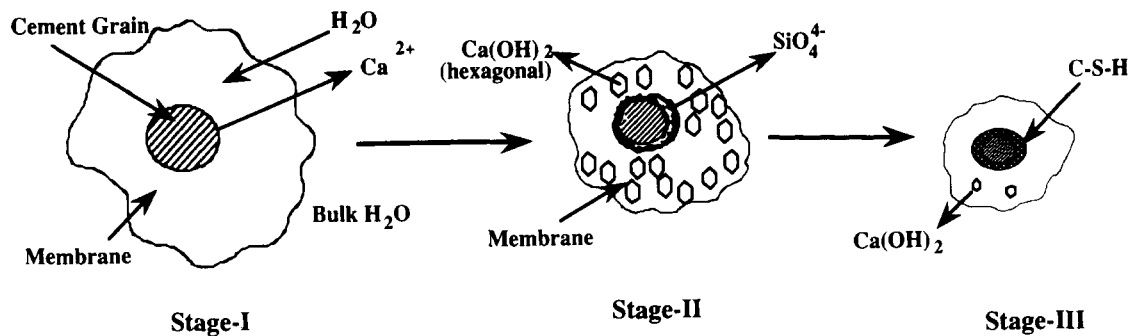


FIGURE 2. Gel model of cement hydration.

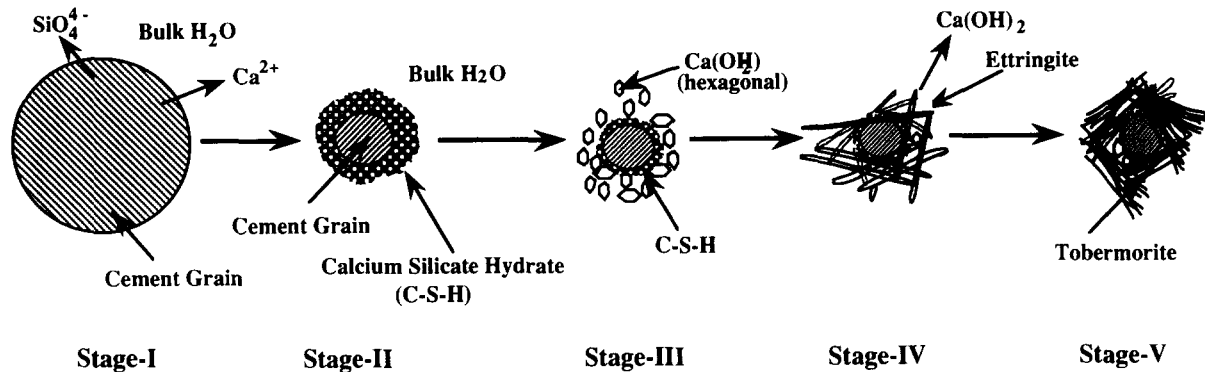


FIGURE 3. Crystal model of cement hydration.

molecules, and outward migration of mainly Ca^{2+} and silicate ions due to the difference of osmotic potential on both sides of the membrane. As a result, an excess of portlandite [$\text{Ca}(\text{OH})_2$] will accumulate on the fluid side of the membrane, and precipitate. At the same time an excess of silicate ions, established on the grain side of the membrane, will produce an osmotic pressure differential on the membrane. This pressure differential causes the membrane to rupture periodically and re-form by extruding concentrated silicate solution. This model has been demonstrated to be useful in explaining the retardation of the setting of cement in the presence of heavy-metal waste.¹⁶ The observed retarding effect is due to the formation of insoluble gelatinous hydroxy-compounds of metal cations with negative charges in an alkaline medium.

The Crystal Model

The crystal model (Fig. 3) assumes that upon mixing cement with water, calcium silicate minerals dissociate into charged silicate and calcium ions. These charged silicate ions then concentrate as a thin layer on the surface of cement grains to prevent the interaction of the cement surface with water. This retards the release of calcium and silicate ions from the cement into water. The initial hydration is followed by nucleation and growth of hexagonal crystals of calcium hydroxide that fill up the spaces and cavities between the cement grains. Meanwhile, particles of

C-S-H precipitate out of water onto the silicate-rich layer on the cement grains and gradually form needles or spines. Eventually needles from different cement grains come into contact with each other to form sheets of tobermorite.¹⁵

A ternary phase diagram (Fig. 4) showing the major products of cement hydration (on the $\text{CaO-SiO}_2\text{-H}_2\text{O}$ phase diagram) has been constructed by Atkinson *et al.*¹⁷ This diagram shows that Ca- and Si-based compositions can be divided into various regions in which an aqueous phase is in metastable equilibrium with a particular solid phase in a hydrating cement system. The aqueous phase in equilibrium with solid phases has a definite composition at a particular temperature and pressure. The shaded area represents the region of C-S-H phase

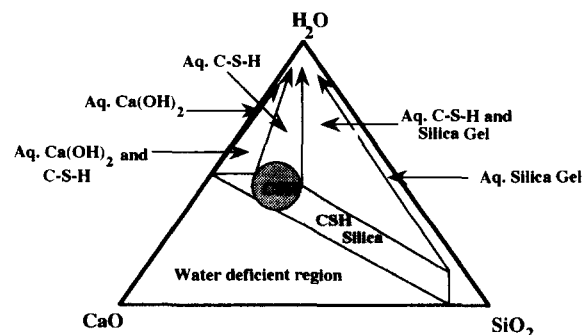


FIGURE 4. Ternary phase diagram of the $\text{CaO-SiO}_2\text{-H}_2\text{O}$ system at 25°C showing different phases at equilibrium. (Aq. refers to an aqueous medium. Adapted from Ref. 17.)

and clearly indicates that its composition is strongly dependent on the Ca/Si ratio. The pH control in such a system has been discussed by Glasser.¹⁸ The highly alkaline nature of the pore solution is considered to be due not only to the presence of Ca(OH)_2 and a high Ca/Si ratio C-S-H, but also to a large extent on the quasi-equilibrium between the solid(s) and aqueous phase(s). It should, however, be mentioned that the presence of pozzolanic materials in cement is expected to lower the pH of the system, since their reactions will remove Ca(OH)_2 as well as change the Ca/Si bulk ratio.

Pozzolans

Pozzolanic materials are also used either separately or as an admixture with cement for s/s purposes. These substances contain SiO_2 , Al_2O_3 , Fe_2O_3 and a small amount of CaO. They are rich in SiO_2 and poor in CaO, while the reverse is true for dry clinker in cement. The mineralogical composition and the relative proportion of various oxides in pozzolans are different from those present in Portland cement. Pozzolanic substances alone are not cementitious, but they may become so when allowed to react with lime and water. When blended pozzolanic cement is hydrated, the clinker compounds react first to produce, among other things, lime. Subsequently, the reactive oxides (e.g. SiO_2 , Al_2O_3 , Fe_2O_3 , etc.) in pozzolans react with lime to produce mainly calcium-silicate-hydrate ($\text{CaO-SiO}_2\text{-H}_2\text{O}$), calcium-aluminate-hydrate ($\text{CaO-Al}_2\text{O}_3\text{-H}_2\text{O}$), calcium-aluminate-silicate-hydrate ($\text{CaO-Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$) and calcium-alumino-ferrohydrates ($\text{CaO-Al}_2\text{O}_3\text{-Fe}_2\text{O}_3\text{-H}_2\text{O}$) phases. These phases have similarities with those obtained after hydration of ordinary Portland cement.

The mechanisms of s/s are complex, resulting from a blending of dynamic cement chemistry with solution equilibria and the kinetic processes, with and without the coupling of many surface and near-surface phenomena. The processes at the surface are central to many important considerations like adsorption, surface complexation and precipitation in s/s phenomena. A clear understanding of these phenomena are needed to formulate a comprehensive mechanism of s/s processes to model these systems and design their improvement for long-term effectiveness. The mutual interactions of the cement and pollutants also need to be determined and incorporated into any detailed chemical models of s/s systems. Little is known about the: (i) adsorption behavior of different metal cations on cementitious materials, (ii) physical and chemical changes that take place as a result of adsorption of these metal ions, (iii) effects of additives, like pozzolanic substances, polymers, etc., on adsorption, and (iv) leaching behaviors of different metal cations adsorbed on these substances. Adsorption of metal pollutants

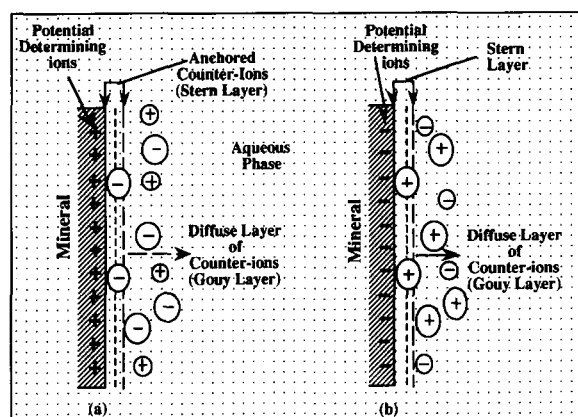


FIGURE 5. Schematic diagram of the electrical double layer at a mineral surface in an aqueous phase; (a) and (b) refer to positive and negative surfaces, respectively.

by cementitious materials is an important area that needs to be addressed for better understanding of the s/s processes.

Adsorption

The adsorption of hazardous cationic metal species from aqueous medium by cementitious substances or by any other minerals and clays is strongly dependent on: (i) chemical characteristics of the surface, (ii) electrical double layer at the solid-liquid interface, (iii) adsorption site densities, and (iv) composition and pH of the medium. The adsorption of metal ions may lead to chemical interactions between molecules on the surface and the ions that are being adsorbed, or the adsorption process may be purely physical in nature. Figure 5 shows that if an ionic species is adsorbed at the mineral surface (solid-liquid interface), then, for electroneutrality, an equivalent number of opposite ions (counter ions) must also be adsorbed to form what is known as the "Electrical Double Layer". An electrical double layer on dispersed particles, in essence, consists of two parts: the first part is close to the surface, and the other is immediately adjacent to the solution. The total surface charge (σ_s) must be equal and opposite to the charge on the solution side (counter charge) so that the electrical double layer, as a whole, is electro-neutral

$$\sigma_s + \sigma_H + \sigma_D = 0 \quad (1)$$

where σ_H and σ_D are the charges in the Stern or Helmholtz layer and the Gouy layer, respectively. The model is called the "Stern Model" or the "Helmholtz Model" and the plane through the center of charges of the counter ions adjacent to the surface is known as the "Stern Plane".

The layer adjacent to the "Stern Layer" is the diffuse double layer of the counter ions which is also known as the "Gouy Layer". An imaginary plane

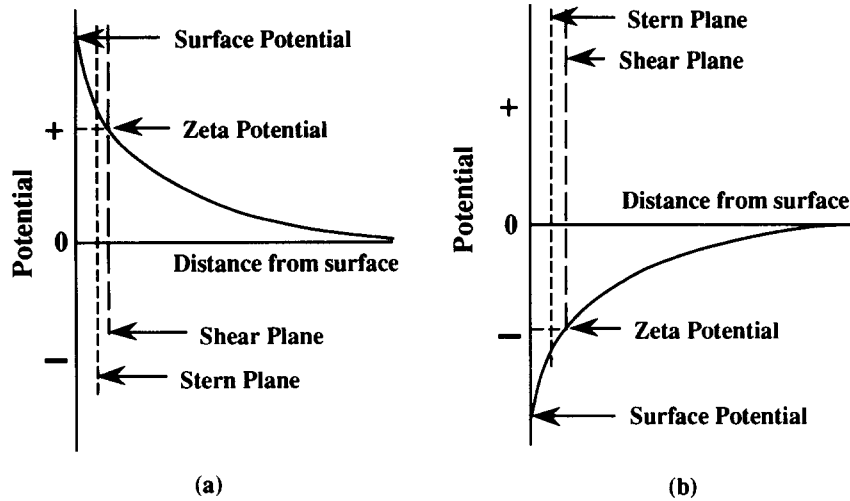


FIGURE 6. Representative plot of the change of potential as a function of distance from the surface.

separating the liquid adhering to the solid surface and the mobile part of the liquid is called the “shear plane”. In the Gouy layer no specific interactions between the surface and the counter ions are envisaged. Since the counter ions have no intrinsic affinity for the surface, they will be subjected to thermal motion and there will be less preponderance of these ions in the regions near the interface than in the case of the electrical double layer. However, the change in potential in moving from the surface to the bulk of the solution through the double layer is schematically shown in Fig. 6, where the potential at the surface is maximal, and it decreases exponentially with the distance from the surface.

Equations describing the distribution of counter ions in a diffuse ion swarm formed at a charged planar surface (Gouy–Chapman diffuse model) have been reported by a number of authors.^{19–21} According to this model the total charge density (σ_p in $C\ m^{-2}$) for a symmetrical electrolyte of ionic charge Z on the surface is related to the surface potential (ψ_d in mV) by the following equation:

$$\sigma_p = (8RT\epsilon\epsilon_0c)^{1/2} \sinh(Z\psi_d F/2RT) \quad (2)$$

where ϵ = dielectric constant of the medium, ϵ_0 = dielectric constant in vacuum ($C\ V^{-1}\ cm^{-1}$), c = molar concentration of the electrolyte, R = molar gas constant, T = temperature in K and F = Faraday constant. If $\psi_d \ll 25$ mV, equation (2) is written as:

$$\sigma_p = \epsilon\epsilon_0\kappa\psi_d \quad (3)$$

where κ is the reciprocal thickness (cm^{-1}) of the double layer and is defined as:

$$\kappa = \{2F^2 110^3 / \epsilon\epsilon_0 RT\}^{1/2} \quad (4)$$

where I is the ionic strength of the electrolyte. As can be seen from equation (2), the total charge density (σ_p) is dependent on the concentration as well as on

the valency of the ions present, whereas the thickness of the double layer is determined by the concentration, ionic size and valence of the counter ions. However, a quantitative consideration of these equations is beyond the scope of the present article and the interested readers are referred to articles cited in other references.^{19–21}

The ions chemisorbed at the surface of the adsorbent constitute the potential-determining ions and these establish the surface charge. The surface charge on an adsorbent surface is determined by the adsorption density of the potential-determining ions. The surface charge (σ_s) for a monovalent salt is given by:

$$\sigma_s = F(\Gamma_{M^+} - \Gamma_{A^-}) \quad (5)$$

where Γ_{M^+} and Γ_{A^-} are the adsorption densities of the potential-determining cations and anions, respectively, and F is the Faraday constant.

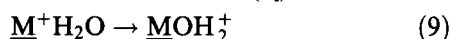
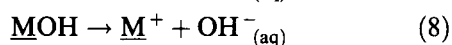
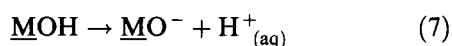
The potential-determining ions (PDI) may consist of ions of which the mineral is composed, H^+ or OH^- and collector ions that form insoluble salts with surface mineral species or complexes on the mineral surfaces.²² For many minerals, such as oxides, PDI are H^+ or OH^- so that equation (5) can be written as:

$$\sigma_s = F(\Gamma_{H^+} - \Gamma_{OH^-}) \quad (6)$$

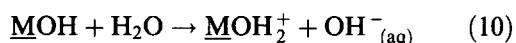
The concentrations of the PDI and the net surface charge are pH dependent. The pH at which the surface charge is zero ($\sigma_0 = 0$) is called the “Zero Point of Charge” (ZPC) of the minerals. The ZPC is a characteristic property of the oxide minerals. When H^+ and OH^- are the potential-determining ions, the ZPC is expressed in terms of pH and it is designated as pH_{zpc} . The pH_{zpc} is an important parameter since it determines the acidity and basicity of the hydrated oxides which control the adsorptive potential of a particular oxide. When $pH > pH_{zpc}$ the surface is

negative, and cations will be adsorbed. Conversely, when $\text{pH} < \text{pH}_{\text{zpc}}$ the surface becomes positive, and anions will be adsorbed. Some authors have preferred, "Point-of-Zero-Salt-Effect" (pH_{pzse}) instead of pH_{zpc} , since "Zero-Point-of-Charge" is independent of ionic strength.^{23,24}

Another term, "The Point-of-Zero-Net-Proton Charge" (pH_{pnzpc}) is also used to indicate the condition of the surface.²⁵ The pH_{pnzpc} corresponds to the pH where the surface is neutral. The ZPC is a significant quantity because the sign of the surface charge is expected to control the s/s of anionic or cationic species. The mechanism of surface charging has been discussed by Park *et al.*²⁶ The reactions which lead to surface charging may be shown by considering metal hydroxide (MOH) and summarized as follows:



Since it is unlikely that a M^+ metal ion alone will exist at the surface, Mott²⁷ proposed the formation or dissociation of a positively charged site by combining reactions (8) and (9) as shown below:

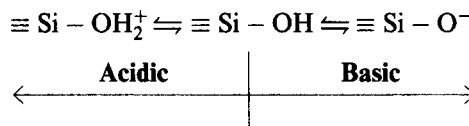


Surface Charges

The adsorption of any species onto a surface is dependent on its surface properties, specifically the surface charge. In the literature four different types of surface charges are recognized:

I. *Permanent structural charge.* This arises due to: (a) lattice imperfections or site vacancy at the solid surfaces, and (b) isomorphic substitution within the lattice. For example, in the case of phyllosilicates,²⁸ trivalent cations may substitute for Si^{4+} or divalent cations may substitute for Al^{3+} in the octahedral structure of crystal lattices to provide a permanent negative charge; or Ti^{4+} may substitute for Fe^{3+} in $\alpha\text{-FeOOH}$ to provide a permanent positive charge.²⁹ These charges are unaffected by pH changes in the environment.

II. *Coordinative surface charge.* The coordinative surface charge arises from chemical reaction involving the surface functional groups. This type of surface charge is dependent on the degree of ionization and pH of the medium. For example, the surface charge on the hydrated silica surface is determined by the pH of the medium and is explained by the acid-base behavior of the silanol group ($-\text{Si}-\text{OH}$) in water:



Most oxides, hydroxides and oxyhydroxides exhibit this kind of amphoteric behavior.

III. *Charges due to inner-sphere complexes.* The adsorption of specifically adsorbed ions, e.g. phosphates, Fe, Zn, etc., on the negative surface will also contribute to the surface charge. These complex ions have H_2O or OH^- groups attached to the ligand sites. Upon adsorption on the negative sites, some of the ligand sites are exposed to the surface providing additional charge sites. The surface properties of the original mineral will be greatly modified. Thus, the bonding energy of the adsorbed ions will vary depending on the nature of the surface. In a heterogeneous system such as cement this type of surface charge may greatly influence the speciation of the toxic metal contaminants. Hence, coating the cement particles with Fe oxides or Mn oxides may increase their binding capacity and affinity for toxic metals.

IV. *Charges due to polymer and surfactant adsorption.* The adsorption of polymers on negative surfaces has been observed.³⁰ These polymers provide potential additional sites for adsorption of organic molecules by processes such as Van der Waal, hydrogen bonding, hydrophobic bonding and London forces. It has been seen that the adsorption of anionic polymers on negative surfaces occurs through the coordination of Ca^{2+} and Mg^{2+} , present on the polymer. There is a critical need to understand the nature of interaction of organic molecules with superplasticizers in cement. Adsorption of superplasticizer molecules on the cement particle's surface will provide sites for adsorption of hydrophobic molecules or mixed wastes that are otherwise not possible to solidify and stabilize.

Acidic and Basic Properties of Oxides

The relative basic and acidic properties of a particular oxide determine the pH at the ZPC. These acidic and basic properties of the oxide in turn are a function of such variables as: (i) cation size and valence, (ii) hydration state of the solid, and (iii) geometrical arrangements of the ions.²⁶ Strong amphoteric oxides, like $\alpha\text{-Fe}_2\text{O}_3$ (ZPC = 8.5) and $\gamma\text{-Al}_2\text{O}_3$ (ZPC = 8.5) have ZPC near neutral pH, while acidic oxides, such as SiO_2 (ZPC = 2.0) have ZPC at a lower pH value since they are proton donors.^{26,31,32} The ZPCs of a complex mixture of oxides, hydroxides and oxyhydroxides are expected to depend on all the various components involved. However, the PDI at the mineral surface will adsorb the counter ions from the solution either by

Coulombic (e.g. electrostatic) attraction or by chemisorption through covalent bond formation.

A knowledge of another electrokinetic phenomenon, zeta potential (ζ), and its variation with solution condition is also important in mineral chemistry. The " ζ " refers to the potential drop between the shear plane and the bulk of the solution medium (Fig. 6). A knowledge of the change of ζ at the mineral-water interface with solution conditions is of fundamental importance in understanding the adsorption phenomena. Anions will be adsorbed when the ζ of a mineral is positive; conversely, cations will be adsorbed when the ζ is negative.³³ However, the point at which the zeta potential becomes zero has special significance. This point is termed as "The Isoelectric Point" (IEP). The zero point charge (ZPC) and/or isoelectric point (IEP) values of minerals/cementitious materials have been considered by many authors^{34,35} to correlate with the adsorption behavior of metal ions. The ZPC and the IEP of most mineral systems are extremely close to each other and may even coincide in many cases, except in the case of specifically adsorbing polyvalent and surfactant ionic species.³⁶

Oxide-Water Interactions

The interactions of metal ions with hydrous oxide surfaces have been extensively studied. The proper-

ties of an adsorbent surface under various conditions are illustrated in Fig. 7.¹⁰ An oxide surface that has been created in vacuum is shown in Fig. 7a. Exposure of this surface to water results in the adsorption of water molecules (Fig. 7b). These can dissociatively chemisorb to produce surface hydroxyls that have both acidic and basic properties (Fig. 7b and 7c). In acidic solution, such as might be experienced in leaching, the basic hydroxyls are removed from the surface, producing Lewis acid sites (L_a) that may lead to a full positive or a partial positive charge. In acidic solutions, the surface can pick up positive charge which restricts cation adsorption and upon leaching can cause basic cation ejection (Fig. 7d). In basic solutions, as commonly found in cement, the surface hydroxyls are deprotonated producing negative oxide sites (Lewis base sites, L_b). The basic hydroxyls remain on the surface, but a net negative charge will develop that restricts anion adsorption to cause anion ejection and to promote cation adsorption (Fig. 7e). These sites can be characterized either by adsorption of ammonia or pyridine molecule on the mineral surface and monitoring it by the Fourier transform infrared spectroscopy (FTIR). Quantitative predictions of the extent of the pH-dependent reversible adsorption have been discussed by numerous authors.^{22,37-40}

When the environment is basic, it can be seen that the surface charge will be negative and metal cations will be adsorbed on the surface. On the contrary, under acidic conditions, the surface charge is positive and anions will be adsorbed. The change of surface charge as a function of pH is demonstrated in Fig. 8. As already mentioned, the point of zero charge corresponds to the pH-value where the net surface charge is zero.

Typical anion and cation adsorption curves as a function of pH are also shown in Fig. 9. Results of Pb, Cu, Zn and Cd adsorption experiments in which metal partitioning between solid and solution phases are varied over wide ranges of pH and concentrations of iron oxide, $\gamma\text{-Al}_2\text{O}_3$ and $\alpha\text{-SiO}_2$, have been reported by Leckie *et al.*⁴¹

The adsorption of anions decreases as they approach the ZPC of the adsorbent and goes to zero beyond the ZPCs of minerals. By contrast, the cation adsorption increases as it moves further away from

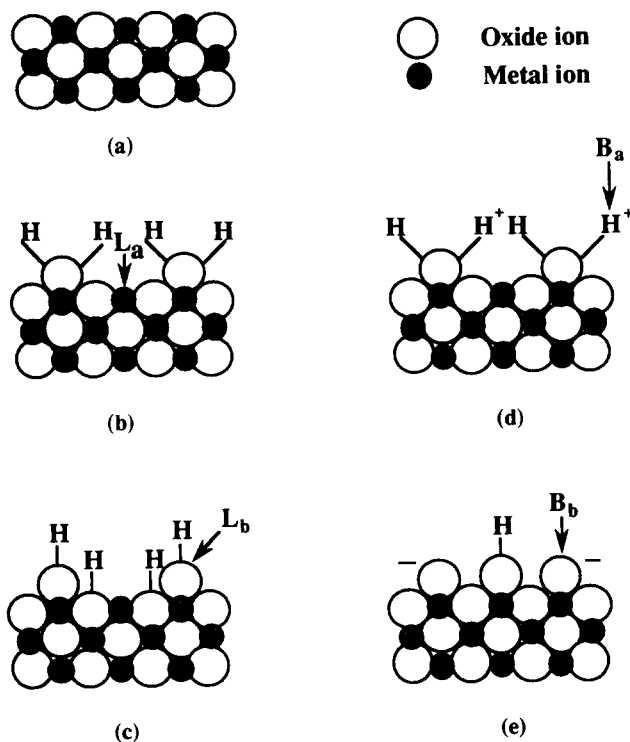


FIGURE 7. Schematic representation of an oxide surface under various conditions: (a) formed under vacuum, (b) with adsorbed water molecules, (c) with dissociatively adsorbed water, (d) in an acidic medium, and (e) in a basic medium. L_a , L_b , B_a and B_b are Lewis acid, Lewis basic, Bronsted acid and Bronsted basic sites, respectively.

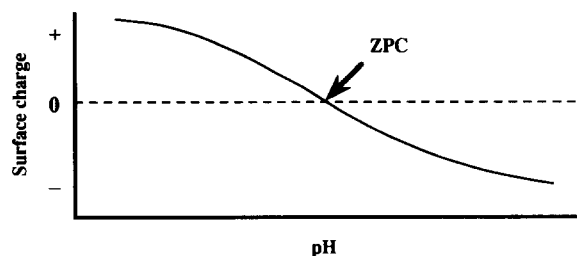


FIGURE 8. Surface charge as a function of pH.

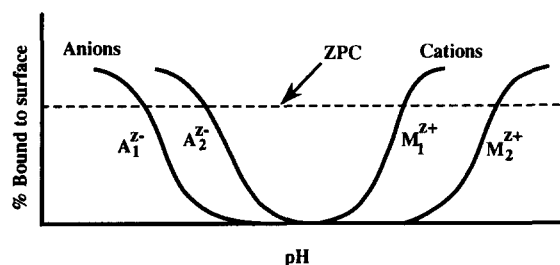


FIGURE 9. The pH response of cation and anion adsorption on hydrated oxide surfaces. M_n^{z+} and A_n^{z-} are metal cations and anions of varying charges, respectively.

the ZPC. Hence, the adsorption of ions is found to be strongly dependent on the pH of the medium and a small shift in pH in surface water can cause a sharp increase or decrease in ion adsorption (Fig. 9). As seen qualitatively in Fig. 8, the curve indicates that under normal pH conditions mixing cement with silica, clay minerals, α -FeOOH or γ -Al₂O₃ oxides that are negatively charged, the cement paste may exhibit a stronger affinity for the positively charged hazardous metal ions. This mechanism has been demonstrated by many authors on a variety of surfaces and these results have been documented in an excellent review by Davis and Kent.²⁵ The Mechanism of s/s is based on the adsorption capability of surface hydroxides and MOH groups which are formed by the dissociative sorption of water molecules.

Surface Complexation Model

Many adsorption-desorption phenomena have been successfully explained by surface complexation methods and numerous models have been proposed over the years.^{39,42,43} These models assume a particular interfacial structure resulting in surface reactions and take into account different electrostatic correction factors to the mass equation. According to Davis and Kent,²⁵ these surface complexation models take the following parameters into consideration: (1) mass balance equation for all the surface reactions, (2) a mole balance equation for surface sites, (3) surface charge computation, and (4) a set of equations representing the constraints imposed on the interfacial phenomena. The surface complexation models commonly found in the literature are: (1) Constant Capacitance Model (CCM), (2) Double Diffuse Layer Model (DDL), and (3) Triple Layer Model (TLM). A detailed discussion of these models are beyond the scope of the present article and the readers are referred to the review by Davis and Kent²⁵ and references therein. The CCM has been used to model the adsorption of low concentration of ions by hydrous oxides,⁴⁴ but recently solutions of high concentrations have also been successfully tested. This model considers the adsorption of ions in

the "Stern Layer" forming inner-sphere complexes. In the DDL, all the ions are adsorbed as coordinative complexes within the Stern layer, and the counter ions are present in the Gouy layer. Since the CCM and the DDL are restricted to only one adsorption plane, they are limited in differentiating strongly and weakly bound ions.

The Triple Layer Model (TLM)

The Triple Layer Model (TLM), with specific counter ion binding at the oxide-water interface, was first proposed by Yates *et al.*⁴⁵ and subsequently developed by Davis *et al.*⁴⁶ for its quantitative applications to oxide-water interface systems. Unlike the Constant Capacitance Model and the Diffuse Double Layer Model, the TLM comprises a surface plane for the adsorption of the PDI (also called inner Helmholtz layer or the α -plane), and a second adsorption plane for weakly bound counter ions (also called the outer Helmholtz plane or the β -plane). According to the TLM, the oxide surface, containing only protons and hydroxide ions in the α -plane, is characterized by a charge density (σ_d) and potential (ψ_0). The charged surface sites, at the innermost plane, lead to specific ion adsorption in the α -plane with characteristics charge density (σ_α) and potential (ψ_α), respectively. The TLM of the oxide-water interface has been used to evaluate the equilibrium partitioning of trace metals and metalloids between sediments and associated aqueous phases.²⁵ However, in cement-based systems the complexity and lack of information on the composition and its rapidly changing nature make the surface complexation approach extremely difficult.

These models describing the interfacial phenomena at the solid-liquid interface are important for a better understanding of the concentration and potential gradient as a function of distance from the surface. However, these models are not intended for understanding the critical role the concentration and potential gradient play in controlling the mechanism of surface reactions in a heterogeneous system. We are proposing a charge control reaction mechanism in cement-based s/s systems to explain the passivation of cement hydration and setting through the formation of bi- and tri-layers in the presence of certain metals and superplasticizers.

The Charge Dispersal Model (CDM)

The speciation of toxic metals in cementitious materials is strongly dependent on the aqueous chemistry of the metal cations in very basic solutions. Retardation of cement setting by Zn, Cd and Pb have been previously reported by a number of authors.⁴⁷⁻⁵⁰ We have recently reported the s/s of EPA priority toxic metals by cement-based systems.^{51,52} In light of these results we have developed a charge dispersal

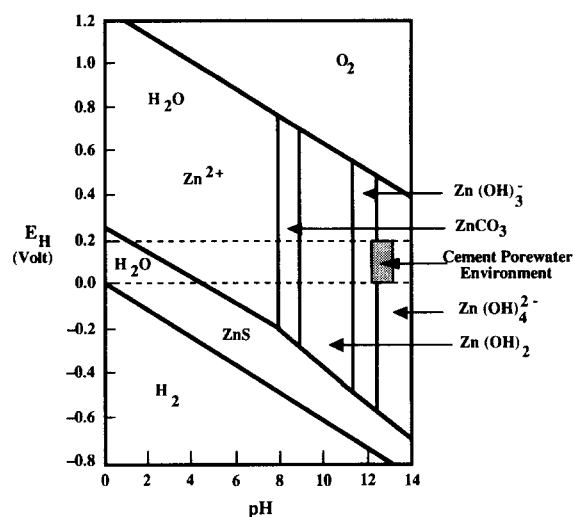


FIGURE 10. Stability of some zinc compounds in relation to E_H (volts) and pH. (Based on Ref. 54.)

reaction model which clearly explains the surface coating and retardation of cement hydration. The adhesive binding agent in hydrated Portland cement is a colloidal calcium-silicate-hydrate (C-S-H) gel. The hydrated cement paste is highly alkaline ($\text{pH} = 13.0 \pm 0.5$) and in this environment the cement surface or the newly formed C-S-H phase will possess a negative charge because the ZPC of the commonly occurring silicate minerals in the cement system is much below the pH (13 ± 0.5) of cement paste. The most abundant counter ions in cement solution are Ca^{2+} cations extruded from inside the hydrating cement clinker through the semi-permeable C-S-H gel membrane which acts as a diffusion barrier after the initial period of hydration reaction. These oppositely charged Ca^{2+} counter ions will immediately surround the negatively charged C-S-H surface and preferentially adsorb, due to their higher charge density, to form a layer of positive charge. The negative surface and the layer of positive charge combine together to constitute an "Electrical Double Layer". The ions forming the electrical double layer are expected to be tightly bound. However, the dispersion of other ions present in such a system is an important parameter to be considered, since this is expected to play a significant role in s/s of metals.

The delineation of this problem will be illustrated with Zn as the doped metal in cement systems. The prominent zinc species dissolved in aqueous systems can be deduced from the E_H -pH diagram shown in Fig. 10. The speciation of Zn as pH is increased follow these sequences:

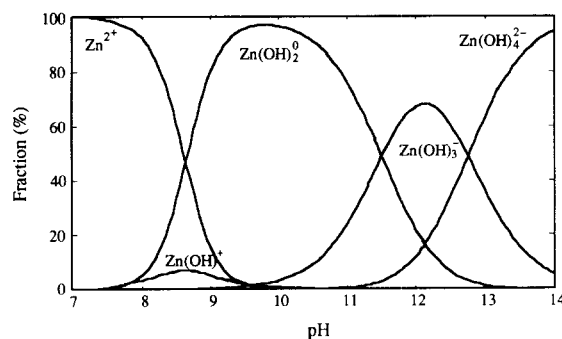
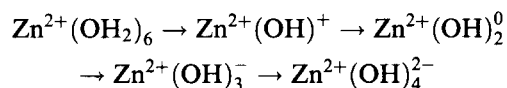


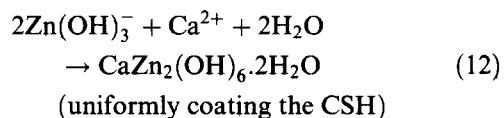
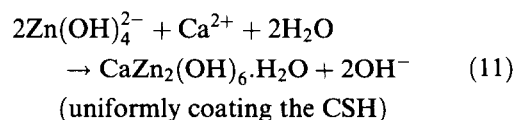
FIGURE 11. Relative concentrations of zinc species as a function of pH.

Theoretical calculations using thermodynamic data published by the National Bureau of Standards⁵³ demonstrate the distribution of relative concentrations of the Zn species in solutions of varying alkalinity. The results of these calculations are presented in Fig. 11.

Between pH 12 and 13, the $\text{Zn}(\text{OH})_3^-$ and $\text{Zn}(\text{OH})_4^{2-}$ anions are dominant species constituting 40% and 60%, respectively (Fig. 11). When $\text{pH} > 13.0$ the $\text{Zn}(\text{OH})_4^{2-}$ ions are the dominant species. The diffuse ion cloud will, therefore, be dominated by OH^- , $\text{Zn}(\text{OH})_3^-$ and $\text{Zn}(\text{OH})_4^{2-}$ ions. However, these ions will be dispersed in a hyperalkaline zone caused by the extraordinary concentrations of OH^- ions, as shown in Fig. 12a.

The negatively charged zinc hydroxy ions would not be expected to adsorb on the negative C-S-H surface. However, the negative surface is charge-compensated by Ca^{2+} ions that form an electrical bi-layer. The next zone in the solution will consist mainly of a diffuse layer of ions constituting what is known as "A Tri-layer of Diffuse Ions" (The Diffuse Ion Swarm). This later layer is composed of mainly $\text{Zn}(\text{OH})_3^-$ and $\text{Zn}(\text{OH})_4^{2-}$ ions. As shown schematically in Fig. 12a, the negatively charged C-S-H surface and the Ca^{2+} counter ions constitute the bi-layer while the C-S-H surface, the Ca^{2+} ions and zinc hydroxy anions form the tri-layer.

The ions contained in the tri-layer are remote from any specific interaction with the surface and are charge-dispersed uniformly over the entire C-S-H surface. This uniform dispersion of zinc anions over the C-S-H surface may lead to the following reactions:



systems. In this article we have reviewed some of the concepts pertinent to mineral-water interface chemistry and brought into perspective the relevant factors that control the chemistry of cement, its hydration and s/s of metals by cementitious materials. The retardation of cement hydration and its subsequent setting by some metals and superplasticizer are due to coating of the cement surface by metal hydroxy and superplasticizer anions, respectively, formed immediately after contact with water. These reactions are dependent on the pH of the hydrating cement paste. The "Charge Dispersal Model" successfully explains this surface coating by calcium compounds and the retardation of cement setting by Zn, Cd and superplasticizer. The formation of calcium hydroxyzincate, calcium cadmate or cement-superplasticizer type complex on the surface is controlled by charge on the surface, and seems to progress by a two-stage mechanism. The negative CSH surface is charge-compensated by Ca^{2+} ions from initial hydration to form an electrical bi-layer, the next zone in solution consists mainly a diffuse layer of metal hydroxy or superplasticizer anions. These ions will constitute a tri-layer of diffuse ions.

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ERRATUM

M. Yousuf A. Mollah, R. K. Vempati, T.-C. Lin and D. L. Cocke. The Interfacial Chemistry of Solidification/Stabilization of Metals in Cement and Pozzolan Material Systems. *Waste Management* 15(2): 137–148 (1995).

Elsevier Science would like to indicate the following changes to the above article and apologise for any confusion that may have arisen from errors printed therein.

p. 137, authors' names: M. Yousuf A. Mollah is the full name of the first author.

p. 139, Fig. 3: Stage-III includes 'Ca(OH)₂ (hexagonal)'.

p. 141, eqn (4) should read: $\kappa = \{2F^2 I I_0^3 / \epsilon \epsilon_0 R T\}^{1/2}$.

p. 144, 2nd para., lines 17 and 18 should read: (2) Diffuse Double Layer Model (DDLDM).

p. 146, eqn (13) should read: $2\text{Zn}(\text{OH})_2^0 + \text{Ca}^{2+} + 2\text{OH}^- \rightarrow \text{CaZn}_2(\text{OH})_6 \cdot 2\text{H}_2\text{O}$.

p. 147: The page range for Reference 2 is 779–789; Reference 17 was published in 1990; the page range for Reference 30 is 13–36.

p. 148: Volume, issue, page range and year of publication for Reference 57 is **25**(3): 682–761 (1995).