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AND ZERO POINT OF CHARGE

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ELECTROKINETIC EFFECTS AND THE CONCEPTS OF ZETA POTENTIAL AND ZERO POINT OF CHARGE*

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Since glass dissolution occurs at a solid-solution (electrolyte) interface, electrochemical concepts such as zeta potential and zero point of charge can be applied to leaching of radioactive waste glasses. Solids** in an aqueous environment are electrically charged.¹ Upon immersion, this charge is balanced by oppositely charged counterions in the solution. The innermost layer of counterions are more tightly bound, while a smaller additional contribution to the neutralization of the surface charge comes from a diffuse ionic distribution in an outer layer. Together these form the electric double layer. The zeta potential is the measured electrokinetic potential between the fixed layer and the outermost layer boundary (Figure 1).

Two types of electric or diffuse double layers can be defined. For convenience they will be referred to as Type I and Type II. The

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**Solids are used in the broad sense including glasses, oxides, hydroxides, and hydrous oxides.

first type can be considered to be due to imperfections or substitutions within the body of a solid, hence producing an electrical charge on the solid surface. The charge is balanced by an excess concentration of ions of opposite charge called counterions. These counterions are attracted to the surface from the surrounding solution. The charged surface of the solid is then considered to be the fixed layer, and the balancing counterions are the mobile or diffuse layer. Together these form the electrical double layer (Figure 2). The second type of diffuse double layer can be considered to be due to specific chemical forces, e.g., ions that are adsorbed at the surface, causing it to become charged. These adsorbed ions are potential-determining ions, and they constitute the fixed layer. The mobile or diffuse layer is made up of oppositely charged counterions as in Type I. Type II diffuse layers are the type most commonly associated with colloids. Since Gouy and Chapman were the first to recognize that the mobile layer was diffuse due to the electrostatic repulsion of the similarly charged ions composing the layer, the diffuse layer is commonly referred to as the Gouy layer. Theoretical treatment of surface charge balancing as a function of the ionic strength of the solution and ionic charge and size is referred to as the Gouy theory (reference 2 for example).

The Gouy diffuse double-layer model predicts³ the following:

1. A preferential concentration of highly charged ions near an oppositely charged surface, e.g., $\text{Ca}^{+2}/\text{Na}^{+}$, concentrations will be high near a negatively charged surface.
2. Increases in ionic strength or concentration of the electrolyte decreases the concentration of highly charged ions in close proximity to the charged surfaces.
3. The ion exchange capacity of a surface comes about from an excess of counterions in the double layer which can be exchanged for other ions.
4. Adsorption of counterions can cause a charge reversal of the surface.

The counterions in the electric double layer can be H^{+} or OH^{-} and, hence, the zeta potential is a pH-dependent parameter. There are several mechanisms by which H^{+} , and OH^{-} , or hydroxo-complexes can determine the surface charge on immersed solid materials. An anhydrous solid can become hydrated by (1) physical adsorption of water molecules (including hydrogen bonding to surface oxygen ions but not dissociation); (2) chemisorption of water which subsequently dissociates, resulting in surface MOH groups; or (3) reaction with the solid forming an oxyhydroxide, hydroxide, or other metal-electrolyte complex.² These mechanisms explain the pH dependence

of the surface charge and the existence of a pH which results in zero net surface charge. This pH value is the pH of the zero point of charge (ZPC) or the isoelectric point of the solid (IEPS)*. Technically, the pH_{IEPS} represents the pH at which an immersed solid surface has zero net charge while the pH_{IEP} represents a pH resulting in electrically equivalent concentrations of positive and negative metal hydroxo-complexes in solution.¹ The isoelectric points of known solids (IEPS) correlate with the isoelectric points of the metal hydroxo-complexes (IEP) in solution.^{1,2}

Previous research⁴ has shown that the leachability of the individual species from a composite waste form is a function of the surface characteristics of the solid monolith. Since the isoelectric point of a solid (ZPC) reflects the chemical composition of the solid and the electrolyte in which it is immersed, then these principles are applicable to glass waste form leaching. The early stages of glass leaching can be envisaged as a process of ion exchange and matrix dissolution. These processes release charged cationic or anionic species at the glass surface, e.g., from the reaction front. Whether these species form hydroxo-complexes which are cationic ($\text{pH} < \text{ZPC}$) or anionic ($\text{pH} > \text{ZPC}$) depends on the pH of the electrolyte (leachant).

* IEPS is defined by Parks¹ as a ZPC arising from the interaction of H^+ and OH^- in the solution with the solid, while the ZPC is the zero point of charge of the surface of the solid. Most authors do not distinguish between the ZPC and the IEPS. Hereafter, only the term ZPC will be used.

The ZPC of a simple solid is related to its cationic charge and the radius of the central ion and is affected by its state of hydration, crystallinity, and impurity concentrations.¹ The ionic potential of an ionic species (ionic charge/ionic radius), has been correlated directly with the ZPC for a wide range of solids¹ and indeed the ionic potential of aqueous hydroxo-complexes is the parameter responsible for the geochemical distribution of elements observed in natural environments.^{5,6} However, it is the structure of the electric double layer, which is absent or collapsed at the ZPC which controls the behavior of near colloidal suspensions or adsorption of the material dissolved from the solid, e.g., surface reprecipitation.

The Gouy model can be used to explain the results of leaching experiments. For example, one observes preferential adsorption of ions with a high charge to radius ratio, e.g., Zr, U, Fe, in the surface gel layers (Table 1). These elements are enriched in the surface layer according to their ionic potential¹¹⁻¹³ regardless of the type of leaching test carried out (Table 1). Relations between ionic strength of the electrolyte and surface elemental concentrations should be an expression of the SA/V parameter of a particular leaching experiment, while the ion exchange capacity should be an expression of the kinetics of diffusion of the ions through the gel layer and through the diffused double layer (reaction layer). Lastly, adsorption of counterions has been found to cause charge

reversals of leached waste glass surfaces and will be discussed in more detail below.

At or near the zero point of charge, when the zeta potential is reduced or ion pair formation occurs, complexes of colloidal dimensions can form. The electrochemical models of the solid-solution interface, therefore, emphasize the physical model of counterion adsorption or colloid destabilization as the surface charge neutralization mechanism. In terms of a leaching model or mechanism, the formation of the charged hydroxo-complexes or colloids could account for the dissolution mechanism, while readsorption of these complexes accounts for surface reprecipitation (back reactions) and subsequent passivation of the leached surface.

The charge on a colloid or hydroxo-complex determines its stability. At the pH of deionized water or natural waters (pH about 7), the complexes listed in Table 2 have the associated charges, while the solid surfaces have the charges indicated in Table 3. Oppositely charged surfaces and hydroxo-complexes or colloids can, and probably do, attract for surface charge neutralization.

Recent zeta potential measurements of SRL165 waste glass indicate that the glass surface is strongly negative (Table 3) over the pH range 4-10. The important components of the reprecipitated layer, such as ferric hydroxide,⁸ are known to form positive hydroxo-complexes (Tables 2 and 3). Hence, negative glass surface potentials attract and bond these complexes onto the leached glass

surface. After leaching, the waste glass has a surface charge characteristic of the adsorbed ferric hydroxide (Table 2), and the leachate has the pH_{ZPC} of ferric hydroxide.⁴ This mechanism explains the stability of the surface layers on waste glass.

The origin of the surface layers appears to be from the dissolution of the solid and is related to the isoelectric point of the solid (ZPC): the ZPC reflects the chemical composition of the solid monolith and the electrolyte in which it is immersed.¹ The pH of the final leachate appears to represent the pH at which the immersed solid surface or the reprecipitated layer has zero net charge. The ZPC, in turn, is related to the cationic charge, radius of the ions, crystallinity, and other properties³ of the immersed solid material. Therefore, the solid controls the ZPC which, in part, controls the pH through the role of the potential determining ions (H^+ and OH^-). At or near the pH_{ZPC} , the electric double layer of near colloidal dimensions is absent or collapsed, and adsorption of metal hydroxo-complexes from the hydrolysis products of the materials dissolved from the solid can occur.

A qualitative picture of the dissolution behavior of nuclear waste solids can be described as dissolution controlled and modified by electrolyte-solid surface reactions. The surface reactions are controlled by the chemical composition of the solid and the concentration of positive and negative metal hydroxo-complexes in the solution which have been derived from the hydrolysis of the

solid. Adsorption of the metal hydroxo-complexes (back reactions)
form surface layers which can be passivating.²⁴

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TABLE 1

Preferential Concentration of Multivalent Ions in Leached Glass Surface Layers

<u>Glass</u>	<u>Elements Enriched in Surface Layers</u>	<u>Leach Test</u>
		<u>Description</u>
Silica Gel ⁷	$Zr^{IV} > U^{IV} \approx Pu^{VI} > U^{VI} > Gd^{III} > Ca^{II}$ $\approx Ba^{II} \approx Na^I$	Order of ion Sorbability
SRL 131 ⁸	Fe, Al, Mn, Mg	MCC-1
SRL 131 ⁹	U	MCC-1
European ¹⁰	U, Ce, Fe	IAEA
Roman ¹¹	$Mg > Fe^{II} > Ca^{II*}$	IAEA
Borosilicate & High Silica ¹²	$Fe^{III} > Ln^{III} > Zn^{II} > Sr^{II*}$	Powdered sample at 70°C
PNL Full Radio- ¹³ active	$Ce > Cm > Pu > Mn > Co > Sr > Ca^*$	----
SRL 21 ¹⁴	Fe, Ni, Mn, Ti, and U	MCC-1
Zn Borosilicate ¹⁵	Zr, U, RE	Soxhlet, 20 mo.
PNL 76-68 ¹⁶	Ca, Sr, Nd, Fe, Zn	MCC-1

* Given as relative retardation on leaching.

TABLE 2

Charged Hydroxo-Complexes in Natural Environments (pH ~7)

Positive

Ferric Hydroxide⁵
Aluminum Hydroxide⁵
Chromic Hydroxide⁵
Titanium Dioxide Hydrate⁵
Thorium Dioxide Hydrate⁵
Zirconium Dioxide Hydrate⁵
Cadmium Hydroxide¹⁷
Cerium Hydroxide¹⁷
Uranium Colloids^{18,7}
Am(III) Colloids⁷
Po(IV) Colloids⁷
Eu(III) Colloids⁷
Y(III) Colloids⁷
Pu(IV) Colloids⁷

Negative

Ferric Hydroxide⁵
Colloidal Silica¹⁹
Vanadium Pentoxide Hydrate⁵
Manganese Dioxide Hydrate⁵
Humus Colloids⁵
Sulfide Sols⁵
Clays⁵
Am(III) Colloids⁷
Po(IV) Colloids⁷
Eu(III) Colloids⁷
Zr(IV) Colloids⁷
Pu(IV) Colloids⁷
Ce(III) Colloids⁷

TABLE 3

Solid Surface Charges in Natural Environments (pH ~7)

<u>Positive</u>	<u>NEGATIVE</u>
$\text{Al}_2\text{O}_3^{21}$	Vitreous Silica ¹⁹
$\text{Fe}(\text{OH})_3^{21,5}$	Vycor Glass ¹⁹
Alumina Tailored Ceramic Waste Form ⁴	Borosilicate Glass ¹⁹
Leached SRL 131* Waste Glass ⁴	Silica ^{5,19}
	Sodium Alumino-Silicate Glass
	Soda Lime Silicate Glass ^{5,19}
	Silica (quartz) ²⁰
	TiO_2^{21}
	Synroc (titania ceramic Waste form) ⁴
	SRL165 Waste Glass ²²

* With hydrated layer enriched in $\text{Fe}(\text{OH})_3$

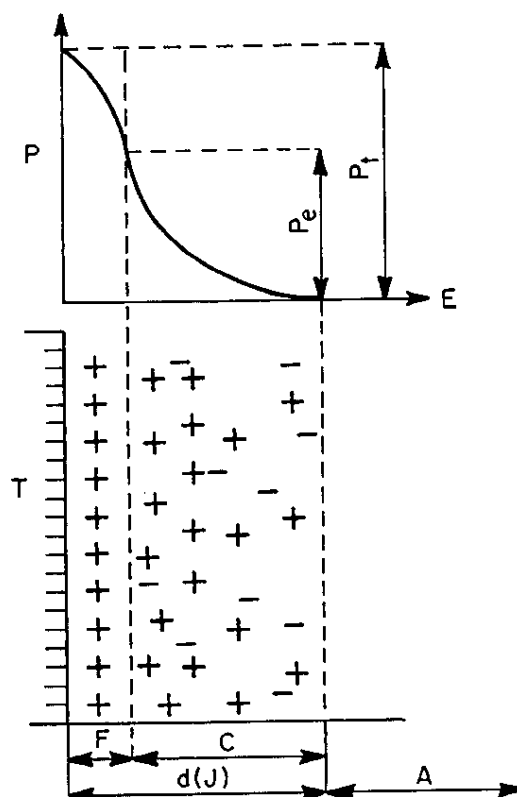


FIGURE 1. Schematic Representation of the Electrokinetic Potential of a Colloid with Negative Charges on the Surface of the Particles

T Particle surface; F Firmly adhering inner layer;
 C Loosely adhering outer layer with diffuse ionic
 distribution; d Electric double layer which also
 corresponds to the interior solution (J); A Exterior
 solution; E Distance from the particle surface;
 P_e Electrokinetic (zeta) potential; P_t Thermodynamic
 potential (after Rosler and Lange, reference 17).

