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MICRO-ELECTROPHORETIC DETERMINATION OF
THE ZETA POTENTIAL OF THORIUM OXIDE

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ABSTRACT

A micro-electrophoresis cell is described and its application to the determination of the zeta potential of thorium oxide is presented. Samples of thorium oxide from different sources, some of which were subjected to certain physical treatments, are characterized by the zeta potential obtained in water. The zeta potentials produced in solutions of HCl, H₂SO₄, KOH, NaOH, Na₄P₂O₇, and Na₃PO₄ are also given.

MICRO-ELECTROPHORETIC DETERMINATION OF THE ZETA POTENTIAL OF THORIUM OXIDE

C. M. Boyd, H. P. House, and Oscar Menis

INTRODUCTION

A test program is being carried out in the Reactor Experimental Engineering Division which involves the use of slurries of thorium oxide, and mixtures of the oxides of thorium and uranium for blanket materials in homogeneous breeder reactors. The various slurry preparations are being examined for pumping characteristics, stability, tendency to form cakes, corrosion and erosion. Those properties of a finely divided solid which affect the stability of the suspensions are, obviously, of primary interest. Among these properties, it was anticipated that the zeta potential would be of considerable importance and interest; consequently, attempts were made to measure the zeta potential of thorium oxide in a number of slurries and, in a few cases, to relate it to the behavior of specific slurries. In the discussion which follows, zeta potential is defined, a method of measurement is outlined, and some test results are presented.

THEORETICAL

When a solid is placed in an aqueous medium, one or more of the following events may take place at the solid-liquid interface: one ion of an electrolyte dissolved in the liquid may be preferentially adsorbed on the surface of the solid; H^+ or OH^- ions may be selectively adsorbed onto the surface; surface atoms or atomic groups may ionize and diffuse away from the solid. As the result of any one of these occurrences, or a combination thereof, an "electrical double layer" is formed adjacent to the surface of the solid and a difference of potential will exist between the surface of the solid and the body of the liquid. If the solid is a very small particle, the particle will, because of its charge,

exhibit many of the properties of ions, e.g., repel particles of like charge and migrate at readily measurable velocities when placed in an electrical field. The magnitude and sign of the charge is of great importance in determining the behavior of colloidal particles, especially in hydrophobic systems.

The double layer was initially compared to a flat, two-plate condenser. The two charges were considered to be concentrated in planes spaced at distances of the order of atomic or molecular dimensions with a linear variation in the potential across the space separating the charged planes. Since the charges on the two planes are equal and of opposite sign, the net charge surrounding the particle is zero. The studies of Gouy⁽⁸⁾ led him to propose a modification of the electrical, double-layer theory, namely, the "diffuse double-layer" theory. According to Gouy's reasoning the outer layer of the double layer surrounding a charged particle extends over a distance greatly exceeding molecular dimensions. Both positive and negative charges are distributed throughout this outer layer, but the charge opposite in sign to the charge on the surface of the particle will predominate in the innermost segment of the outer layer. The predominance of this charge will decrease rapidly as the distance from the surface of the particle increases and approaches zero asymptotically at infinite distance. In the modern theory, developed by Stern,⁽¹⁹⁾ it is assumed that the inner layer of an electrical double layer is immediately adjacent and fixed to the particle surface while the outer diffuse charged layer is movable. The potential drop across the outer movable layer is the electrokinetic or zeta potential. This potential is of primary importance in electrokinetic phenomena. Although Helmholtz⁽⁹⁾ did not postulate a precise structure for the electrical double layer, he developed the following equation for relating zeta potential (ζ) to the velocity of migration (V) of the particle in an electrical field of potential gradient (E),

$$V = \frac{\zeta E}{4\pi\eta} \quad (1)$$

Where: ζ = zeta potential, esu

E = potential gradient, esu per cm

η = viscosity of medium, poise

V = velocity of migration, cm per sec

Perrin⁽¹⁵⁾ later found that the migration velocity was proportional to the dielectric constant (D) of the medium. He, therefore, modified the Helmholtz equation as follows,

$$V = \frac{\zeta ED}{4\pi\eta} \quad (2)$$

According to equation (2), the electrokinetic mobility of the particle is independent of size and shape. Debye and Hückel⁽⁴⁾ concluded that the factor $1/4\pi$ applies only for a cylindrically shaped particle migrating in the direction of its axis and that a different factor, $1/6\pi$ should be used for spherically shaped particles. Henry⁽¹⁰⁾ made a thorough study of the problem and came to the conclusion that shape does not influence the migration velocity of non-conducting particles, if the radii of the particles are large in comparison to the thickness of the double layer. He, therefore, decided that equation (2) is valid for all particles of microscopically visible size.

A number of electrokinetic phenomena are directly related to and occur as a consequence of the formation of the electrical double layer. These phenomena include electrophoresis, electroosmosis, streaming potential and sedimentation potential. Electrophoresis is defined as the migration of charged particles when a potential gradient is impressed across a suspensoid. Electroosmosis (the reverse of electrophoresis) is the migration of the liquid phase under a potential gradient when the suspended, charged particles are restrained from moving, e.g., by means of a porous diaphragm. Streaming potential is the potential difference which is developed between the solution at the ends of a

porous plug or bundle of capillaries when liquid is forced under pressure through the plug or capillaries. Sedimentation potential, the reverse of streaming potential, is the difference of potential produced between an upper and lower stratum of a liquid when charged particles pass through the liquid under either gravitational or centrifugal force. Many investigators have made use of the methods of electrophoresis and streaming potential for the determination of zeta potential. Only the former has been used in this laboratory for this purpose. The detailed discussion of the determination of zeta potential will, therefore, be limited to the application of an electrophoretic method.

In all electrophoretic methods for the determination of zeta potential, the rate of migration of charged particles is measured under a known and fixed potential gradient. The methods for making this measurement are (1) the transference method, (2) the moving boundary method, and (3) the micro-electrophoretic method.

The transference method, which was first introduced by Duclaux,⁽⁶⁾ is similar to the well-known Hittorf method for the determination of ionic mobilities. In this method, a determination is made of the mass of particles which, under the influence of an electrical field, migrate from or into one electrode chamber of a Hittorf-type transference apparatus. The accuracy of this method is subject to the limitation of measuring small changes in concentration and by disturbing factors, such as electrode reactions.

The moving boundary method, which was first used with colloid systems by Picton and Linden,⁽¹⁶⁾ involves the application of an electric field to a suspensoid in contact with an electrolytic solution free of suspended particles and measurement of the rate of migration of the boundary between the suspensoid and the electrolytic solution. In the application of this method in its simplest form, a U-tube is partially filled with a suspensoid and covered with a quantity

of electrolyte. Inert electrodes are placed in the electrolyte in each end of the U-tube, a potential is applied to the electrodes and the rate of migration of the boundary layer is measured. From the rate of migration under a known potential gradient, the zeta potential can be calculated. This method is tedious, time-consuming and, furthermore, a number of conditions related to suspension concentration limit its applicability.

In the micro-electrophoretic method, the movement of individual particles in an electrical field is observed and the velocity of migration is measured by means of a microscope or ultramicroscope. This method offers several advantages over the other methods previously discussed for the determination of zeta potential. The mobility of the particles may thus be determined without modification of the original suspending medium other than diluting it or, if desired, the measurement may be made in a wide variety of other media. It is unnecessary to separate the particulate matter from the medium in which it is suspended and to compact it into a porous plug as is necessary in the application of the streaming-potential method. The time required for a measurement is of the order of only a few minutes compared with several hours for the moving-boundary method. Changes in the medium due to electrode reactions are small or negligible since only a few seconds are required to make the necessary observations and the point of observation is not near the electrodes. The method does, however, involve some complications which must be carefully considered and circumvented.

The suspension is ordinarily placed in a horizontal glass tube, of small cylindrical bore, which is of the order of 20 cm in length. Electrodes are placed at each end of the tube and the movement of particles is then observed in the central section of the tube under a known potential gradient. An electrical double layer is set up at the glass-liquid interface; consequently, when a voltage is impressed across the electrodes the liquid near the walls of the

capillary will flow due to electroosmosis. Since the system is closed, the liquid flowing near the walls of the capillary must return through the central portion of the tube. Thus, levels must exist where the electroosmotic and return flows are balanced. Electrophoretic movement of the suspended particles can be measured directly, uncomplicated by electroosmosis, at these levels of no liquid flow. From theoretical considerations of the flow profiles, Smoluchowski⁽¹⁸⁾ has shown that the level of no-liquid flow is located at a distance from the wall of 0.1465 times the diameter of the capillary.

The micro-electrophoretic measurement of zeta potentials has been carried out in a number of cells differing in style. Cells of rectangular cross-section have been used by several workers.^(2,3,5) On the other hand, cells of cylindrical cross-section have been preferred by others,^(1,7,11,12) since the theoretical treatment of flow in a rectangular cell is complex unless the ratio of the width of the cell to the depth is great. The double-tube cell of Smith and Lisse,⁽¹⁷⁾ in which electroosmotic back-flow does not occur in the observation tube, has the advantage that the electrophoretic velocity is measured at the center of the tube where there is no-liquid flow and where the velocity gradient with depth is zero.

Some cells are designed to use reversible electrode systems such as $\text{Hg-Hg}(\text{NO}_3)_2$, Ag-AgCl , and Cu-CuSO_4 . With electrodes of this type, it is quite probable that some of the electrolyte associated with the electrode will be transferred to the suspension under observation. Any small variation in electrolyte concentration introduces errors in the mobility measurement, especially when electrophoresis is being conducted in solutions of low ionic strength. For this reason it is important to use some simple electrode such as platinum. The use of a platinum electrode, which is polarizable, does not normally cause difficulties since in solutions of low ionic strength the current flow is low.

The electrophoretic movement of the particle is measured by use of a microscope having an eyepiece provided with a scale for measuring the distance through which particles move. Magnification of the order of 100 diameters is usually satisfactory. The particles may be illuminated on the principle of the ultramicroscope, the source of light being at a right angle to the line of observation.

Considerations of the possible systems described above resulted in the choice of the micro-electrophoretic method, in which a cell of cylindrical cross-section and platinum electrodes are utilized for determining the zeta potential of thorium oxide.

EXPERIMENTAL

Apparatus

The micro-electrophoresis cell, shown in Figure 1, is of the cylindrical, cross-section type. It is constructed in three sections of thick-walled Pyrex glass tubing, approximately 8 mm O.D. with a bore of 2.06 mm (calculated from the measurement of the length and weight of a column of mercury placed in the tube). The central section is a straight tube 10 cm in length, terminating in ball joints whereby two L-shaped, end sections are attached, normally with the open ends in an upright position. The ends can be rotated downward for draining the cell. The two platinum electrodes are placed in the end sections, extending downward to the constriction in each section. The total distance between the electrodes is 19 cm; therefore, when a potential of 190 volts is impressed across the electrodes, the gradient is 10 volts per cm. In the mid-portion of the center section, two flat surfaces at right angles to each other were prepared by grinding and polishing the walls of the tubes to within 0.1 mm of the inner surface. Light enters the tube from the side through one of the flat surfaces while the microscope is focused through the other.

FIGURE 1. MICRO-ELECTROPHORESIS CELL FOR ZETA-POTENTIAL

The microscope is an AO Spencer Metallurgical Microscope fitted with a 16 mm (10X) objective, having a working distance of 7 mm, and a 5X ocular containing a micrometer scale. Using these lenses, the scale in the ocular was calibrated with a stage micrometer and one division on the ocular scale was found to be equal to 36 microns. The mechanical stage is fitted with a wood block to which the electrophoresis cell is attached by means of coil springs. The vertical illuminator was removed from the barrel of the microscope and attached to the mechanical stage together with a 5X objective lens, in such a manner as to focus the light onto the bore of the tube, perpendicular to the line of observation.

The source of the D.C. potential, which is applied to the electrodes, is an Oregon Electronic (Model A3A) variable-voltage, regulated power supply. Potentials up to 300 volts may be applied to the electrodes through a reversing switch. The applied potential is measured with a previously calibrated panel voltmeter.

Procedure

The electrophoresis cell must be kept absolutely clean, since materials adhering to the surface of the glass might give different charges to different parts of the tube, causing an irregular electroosmotic type of flow of the liquid. The cell is cleaned frequently with a good detergent or with a sulfuric acid-chromic acid solution, after which all traces of electrolyte is removed by rinsing the cell repeatedly with water. The cell is cleaned between tests involving different samples of thorium oxide or different media. This can be carried out conveniently by utilizing a "pipe cleaner."

Dilute suspensions of ThO_2 , suitable for measurement of zeta potential are prepared by dispersing approximately 0.1 g of sample - either a solid or slurry - in 100 ml of deionized water or in an electrolyte of the desired concentration and pH. The suspension must be sufficiently dilute so that the migration of a

single particle can be followed without difficulty. Portions of the sample are transferred to the cell by means of a dropper. The prepared suspensions are stored, preferably, in polyethylene bottles fitted with screw caps.

A potential of 190 volts is impressed across the platinum electrodes by means of the regulated power supply. The migration of the particles is then measured in the layer which is at a distance from the wall of the bore of 0.1465 times the diameter of the bore. To focus the microscope on this particular point, a correction must be made for the refraction of light by the suspending liquid (water). The equation for the calculation of this correction is,

$$p = x/n \quad (3)$$

Where: x = vertical distance from wall of cell bore

n = index of refraction of suspending liquid

p = vertical displacement of microscope from wall
of cell bore

The bore of the cell used in these experiments was found to be 2,060 μ in diameter. The annular layer, therefore, in which particle displacement is to be observed is located $0.1465 \times 2,060$ or 302 μ from the inner wall of the tube. The vertical displacement of the microscope which is required to bring the layer into focus is, from equation (3), $302/1.342$ or 225 μ , measured from the inner wall of the tube. The microscope is positioned as follows: After centering the bore in the field of view, the microscope is focused on the inner wall of the tube. This is accomplished by locating the position at which the first particles of suspension are observed. The microscope barrel is then lowered 225 μ by means of the micrometer screw.

The electrophoretic velocity of the particles is measured by choosing a particle which is in focus in the center of the field and measuring the time required for the particle to move across 10 or 20 subdivisions of the ocular

micrometer scale. The longer distance is used for the faster moving particles. The time intervals are measured to the nearest 0.1 second with a stop watch. One measurement is made, after which the applied potential is reversed and a second measurement is made. This procedure is repeated five times with re-suspension and re-focusing between each two measurements. The 10 time intervals are averaged from which the velocity in microns per second is calculated. The rate of migration should be measured before sedimentation is appreciable or after re-suspension is accomplished by forcing the column of suspension back and forth in the tube with air pressure from a rubber bulb.

The zeta potential of the particles is calculated from the migration velocity by equation (2), which is written in the following form:

$$\zeta = \frac{300 \times 300 \times 10^{-4} \times 4 \pi \eta V}{ED} \quad (4)$$

Where,

ζ = zeta potential, volts

η = viscosity, poise

V = migration velocity, microns/sec.

E = potential gradient, volts/cm

The constants 10^{-4} , 300 and 300 are necessary conversion factors, since V is in microns rather than centimeters and ζ and E are in volts instead of electrostatic units.

For the specific conditions under which zeta potential was measured, the equation can be simplified to:

$$\zeta = 1.30 \times 10^{-3} V \quad (5)$$

The constant, 1.30×10^{-3} , includes not only the conversion constants of equation (4) but 3.14 for π , 0.009 for η (the viscosity of water at 25°C), 10 for E and 78 for D (the dielectric constant of water at 25°C).

The sign of the zeta potential is determined by the direction of migration. The charged particle will migrate toward the electrode having an opposite charge. It should be remembered that when viewing through a microscope, the true direction is the reverse of that observed.

Table I

Zeta Potential of Thorium Oxide Suspended in Various Electrolytes

Conditions: ThO₂, D-17, thorium oxalate ignited at 650 °C
 Potential gradient 10 v/cm
 Concentration of electrolytes 10⁻⁴ M

<u>Medium</u>	<u>Electrophoretic Velocity, μ/sec</u>	<u>Zeta Potential, mv.</u>
Average of 10 Measurements		
H ₂ O		
Test A	31	+ 40
Test B (initial)	36	+ 47
after 10 min.*	30	+ 39
after 2 hr.*	22	- 29
HCl	60	+ 78
KOH	46	- 60
Na ₄ P ₂ O ₇	46	- 60
Na ₃ PO ₄	90	-117

* Exposure to atmosphere; it is presumed that CO₂ absorption causes the change observed in zeta potential.

Table II

Zeta Potential of Various Samples of Thorium Oxide in Water
and the Effect of Certain Physical Treatments

<u>Thorium Oxide</u> *	<u>Zeta Potential, mv</u>
LO-3	- 39
LO-5	- 42
LO-8	- 36
LO-10	- 40
LO-12 and 13	- 94
LO-13	- 16
LO-7-800	+ 39
LO-7-800 (micropulverized)	+ 21
LO-7-800 RF	0
LO-7-800 RF (micropulverized)	0
LO-7-1000 RF	0
LO-7-1000 RF (micropulverized)	+ 35
LO-7-1600 RF	0
LO-7-1600 RF (micropulverized)	+ 22
LO-2A	+ 35
LO-2A (pumped in loop)	+ 26
LO-2A (blended)	- 23
LO-2A (autoclaved at 250° C)	-130
LO-14	+ 53
LO-14 (pumped in loop)	+ 9
LO-14 (blended)	- 20
LO-14 (autoclaved at 250° C)	- 44

* These thorium oxides were prepared by reacting $\text{Th}(\text{NO}_3)_4$ (Lindsay Chemical Co., Code 103) and reagent-grade oxalic acid at 70° C followed by ignition of thorium oxalate at 800°C for 4 hours.

DISCUSSION

The zeta potential of the thorium oxide, D-17, prepared by reacting $\text{Th}(\text{NO}_3)_4$ and oxalic acid followed by ignition of the thorium oxalate to 650°C for 2 hours, was found in two tests to be +40 and +47 mv in distilled water. After the suspension of oxide was exposed for a period of 10 minutes to the atmosphere of the room, the zeta potential was found to have changed from +47 to +39 mv. Several hours of exposure resulted in a zeta potential of -29 mv. This change was attributed to the adsorption of carbonate derived from the dissolution of CO_2 from the air. When the suspension was protected by storing it in a polyethylene bottle no significant change of zeta potential was observed over a 24-hour period. A zeta potential, varying from +23 to +49 mv in water, has also been reported by O'Connor^(13,14) for thorium oxide ignited to 1700°C . A streaming-potential technique was used by O'Connor to obtain these values.

The positive zeta potential of thorium oxide in water has been interpreted by O'Connor in terms of the ionization of surface hydroxyl groups of a base produced by the hydration of the oxide surface. The hydroxyl ions move to the diffuse layer, thus leaving the surface with a positive charge. The positive zeta potential is increased by HCl and HNO_3 in low concentrations, due to anionic exchange of the chloride or nitrate with the hydroxyl groups, thus resulting in the formation of salts which are more strongly dissociated than the weak base. The normal basic dissociation may be repressed by the addition of hydroxyl ions, e.g., from KOH , thereby reducing the zeta potential to zero. Cationic exchange of the hydrogen of the surface hydroxyl groups can then be effected, with the formation of a more strongly dissociated salt. With an increase in KOH concentration the zeta potential can, therefore, be made negative. Negative zeta potentials were also reported with $\text{Na}_5\text{P}_3\text{O}_{10}$ solutions. It was postulated that

anionic exchange of hydroxyl by polyphosphate groups and anionic adsorption are the major processes which determine the zeta potential. The zeta potentials for thorium oxide in a variety of electrolytes, as determined by the micro-electrophoretic method and listed in Table I, are in agreement as to sign and magnitude with those reported by O'Connor.

Measurements were made of the zeta potential of different samples of thorium oxide in water for the purpose, if possible, of correlating the potential with particular characteristics of the slurries which were observed when these mixtures were circulated in test loops. Of particular interest, was the difference in behavior noted for the oxides designated as LO-2A and LO-14. These oxides had been prepared under identical conditions, contained essentially the same amounts of impurities and were found to have the same particle-size distribution and surface area; when circulated in a test loop, however, these oxides behaved quite differently. The LO-14 oxide tended to form a cake whereas the LO-2A oxide did not. The zeta potential of the LO-14 oxide before circulation was +53 mv as compared to +35 mv for the LO-2A oxide, as shown in Table II. After circulation in a test loop, the zeta potential of the LO-14 material was reduced to +9 mv while that of the LO-2A material was reduced only to +26 mv. The low zeta potential of +9 mv would be favorable for flocculation and cake formation. Therefore, from that standpoint, conditions tending to cause cake formation existed during the circulation of a slurry of this oxide while no cake formed in the slurry prepared from LO-2A oxide. The reason for these differences in zeta potential is not known.

After agitating LO-2A and LO-14 thorium oxides in a Waring blender and heating them in an autoclave, these oxides were found to have negative zeta potentials. It is believed that this has come about as a consequence of the introduction of some contaminant during processing.

A study was made of the effects of ignition of the oxide on the zeta potential. The data are presented in Table II. The zeta potential of L0-7 oxide ignited at 800°C was found to be +39 mv. Portions of this material were then re-ignited at 800°C for 12 hours and at 1000°C for a like period of time, and also at 1600°C for four hours. In each case the zeta potential of the ignited oxide was found to be zero. The ignition, at high temperatures especially, might be expected to reduce the tendency for the oxide to hydrolyze and thus reduce the zeta potential. It was not anticipated, however, to find that a second ignition at 800°C reduces the zeta potential to zero. When the re-ignited oxide was passed through a micro-pulverizer the positive zeta potential was partially restored, except in the case of the material re-ignited at 800°C . This restoration of the zeta potential may be due to the formation of new active surfaces at which hydrates can be formed by hydrolytic reaction.

The zeta potential was found to be a function of pH (see Figure 2). Three different batches of thorium oxide were used to prepare slurries in solutions of sulfuric acid and sodium hydroxide. The pH of the slurries ranged from about 2 to 12.4. In all cases, as the three curves in Figure 2 indicate, the zeta potential was negative with minimum values in the range of pH 5 to 6. As the acidity or the alkalinity of the solution was increased, the negative value of the zeta potential increased rapidly.

It must be recognized that an explanation of the pH-zeta potential relationship is complicated by the fact that adsorption of ions affects pH as well as the zeta potential. For instance, upon addition of thorium oxide to solutions of pH 2 and 3 the pH was changed to 2.1 and 3.2, respectively. Solutions originally at pH 4 changed to pH values ranging from 5.3 to 6.3. When the oxide was added to water (pH 6.1) the pH of the resultant slurries ranged from 6.7 to 6.9, while the pH of initially alkaline solutions was not changed in any measurable

FIGURE 2. EFFECT OF H₂SO₄ AND NaOH ON ZETA POTENTIAL

extent. It can be postulated that in the more acidic slurries sulfate is selectively adsorbed, causing the zeta potential to become more negative. Likewise, in strongly alkaline solutions, the adsorption of hydroxyl ions will have the same effect. According to the theory of the electrical double layer, a quantity of hydrogen ions equivalent to the sulfate adsorbed will be concentrated in the outer diffuse layer. These hydrogen ions will be under a restraint which will, in effect, lower the hydrogen-ion activity so that the indicating electrode of the pH meter will detect fewer ions per unit volume, consequently, the observed pH will be higher than it would have been in the absence of the oxide.

SUMMARY

The micro-electrophoretic method is satisfactory for the measurement of the zeta potential of thorium oxide. A specific characteristic zeta potential cannot be assigned to thorium oxide as samples of relatively pure oxide from different sources suspended in distilled water were observed to have different positive zeta potentials. The magnitude and even the sign of the zeta potential were apparently changed by relatively small amounts of contaminants introduced into thorium oxide during preparation or processing. This fact must be considered in using zeta potentials measured in water to characterize the oxide or in evaluating the effect of diverse physical treatments.

In electrolytes such as HCl, which react with thorium oxide to produce highly ionized salts, the zeta potential is positive. When, however, the oxide is suspended in an electrolyte, such as KOH or Na_3PO_4 , which repress the normal dissociation of surface hydroxyl ions and from which anions are adsorbed, a negative zeta potential is observed.

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