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DATE FEB 14 1957 *DE*

For The Atomic Energy Commission

W. R. Canale
Chief, Declassification Branch

COMMENTS ON THE EFFECT OF ELECTROLYTES ON
THORIUM OXIDE SLURRIES

OBJECTIVE

The physical properties of thorium oxide slurries are very sensitive to the species and quantity of electrolyte present. The proper combination of these will impart desirable physical properties to the slurry. It may be necessary to add electrolyte to the slurry to improve the action of the internal catalyst and to decrease the corrosion-erosion properties of the system. The object of this report is (1) to point out the necessity of a basic understanding of the action of the electrolytes; (2) to suggest that a study of the ionic atmosphere around the thorium oxide particles will provide the basis for this understanding; and (3) to describe several methods of studying the changes in the structure of the ionic atmosphere caused by the addition of electrolytes. These methods should be useful over a wide range of temperatures and give results of a truly general nature.

ENGINEERING IMPORTANCE

The specifications of a thorium oxide slurry blanket for the HRT is complicated by the fact that the blanket must fulfill many diverse requirements. These include: (1) having satisfactory rheological properties over a temperature range of from ambient to 300°C; (2) of minimizing the sedimentation, the corrosion, the erosion and the radiation damage problems; and, (3) the desirability of having an internal recombination catalyst. These problems are currently being examined on an individual basis. However, for successful operation of the HRT blanket the solutions

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to these problems must be compatible with each other and cannot be mutually exclusive. A common factor possessed by several suggested solutions to these problems is the addition of different electrolytes to the system.

It has been shown that at room temperature the electrolyte atmosphere has a most striking effect on the apparent viscosity of a thorium oxide slurry.⁽¹⁾ This is of importance in startup and shutdown procedures. However the addition of an electrolyte, such as sodium silicate,⁽²⁾ at the start of a loop test has not resulted in improved handling characteristics during the run. As yet this has not been satisfactorily explained.

Loop tests have shown the desirability of the presence of sulfate ion both from the handling viewpoint⁽³⁾ and from the desirability of minimizing the corrosiveness of the slurry.⁽⁴⁾ Possible internal catalysts may require the use of an electrolyte such as sulfuric acid.⁽⁵⁾ The optimum sulfate ion concentration for use with catalysts does not necessarily coincide with the best value from the handling viewpoint.

As much as 1000-10,000 ppm of impurities, such as barium, lanthanum, cerium, carbonate, etc., have been found in thorium oxide.⁽⁶⁾ No information is available on the possible effects these impurities will have on the slurry physical properties.

The ionic atmosphere of thorium oxide particles in a circulating system will be continuously changing because of the production of corrosion-erosion products. Analytical data from the loop tests show that essentially all of the corrosion-erosion products are adsorbed on the thorium-oxide particles.⁽⁷⁾ As yet there is no evidence showing what effect these adsorbed materials will have on the handling characteristics of the slurry.

The engineering design and specification of the blanket must incorporate solutions to all these problems. A fundamental understanding of the action of electrolytes is necessary in order to design specific engineering experiments testing the use of electrolytes for the solution of problems in the HRT slurry blanket.

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ANALYSIS OF THE PROBLEM

The electrical double layer concept has been used to explain many different phenomena. Specific examples will be chosen to illustrate the wide range of problems involving the electrolyte atmosphere around a particle that have been studied using the electrical double layer concept. These include: studies on the flocculation of hydrophobic materials, an explanation of some of the rheological properties of materials, and prediction of the effective particle size due to the presence of a double layer.

A qualitative picture of the double layer may be obtained from the following considerations. Experimentally it is known that in suspensions of solids the particles are electrically charged. Since the suspension as a whole is neutral, an equal charge of opposite sign must be present in the suspending medium. Because of the attraction of charges of opposite sign, charge and counter charge remain close to each other, giving rise to the so called "electrical double layer."

In studies of the flocculation of hydrophobic materials, it has been shown that the addition of electrolyte did not discharge the particles. Instead the charge density and thickness of the electrical double layer were changed, allowing flocculation to take place. (Parenthetically it may be pointed out that based on this model, any action of ionizing radiation upon the handling characteristics must involve a change in the surface properties of the thorium oxide. This follows since, for a constant electrolyte concentration, it is only the surface properties that determine the structure of the electrolyte atmosphere.)

In rheological studies, a direct relationship has been shown to exist between the structure of the electrical double layer and the viscosity of suspensions. (The electro-viscous effect to be discussed later.) Also, sediments of highly charged particles have been shown to flow like a

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Newtonian fluid under very low rates of shear. However, flocculated sediments often show behavior very similar to a Bingham plastic. The electrical double layer concept also provides a possible explanation of the thixotropy of some suspensions. If the potential of the particle double layer is reduced sufficiently, then, when the suspension is allowed to stand, the particles will stick together to form a loose network structure, a behavior characteristic of thixotropic materials.

In studies of the effective particle diameter, it has been shown that for a particle 20 Å in diameter having a net charge of 20 units in the electrical double layer, the probability of finding another similar particle within a distance of 80 Å is negligible. Thus the effective diameter of the particle plus double layer is nearer 60 Å than 20 Å.

Many other studies have been made showing the usefulness of the ionic atmosphere and electrical double layer concepts in understanding the action of electrolytes upon suspension of solids in liquids.

Several techniques are available for studying the electrolyte atmosphere around solids in suspension. These include the conductance, and such electrokinetic techniques as: electro-osmosis, streaming potential, electrophoresis and the migration potential.

The measurement of conductance is straight forward and the results yield information about the number of ions in solution as well as about the total charge present on the surface of the particles.

The selection of one of the electrokinetic techniques can be based on the ease of making the test or of interpreting the results. This follows from the fact that a common factor that may be derived from all measurements of electrokinetic phenomena is the zeta-potential.* When

* The electrolyte atmosphere around a particle is considered as being made up of an electrical double layer, the zeta-potential being the potential difference over the mobile part of the double layer. The zeta-potential concept is described in more detail in Weiser,⁽¹⁰⁾ pp 226-232, Alexander and Johnson,⁽¹¹⁾ pp 296-300 or Kruyt,⁽⁹⁾ pp 78, 197.

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compared on that basis the results of the different measurements are entirely compatible.

BRIEF LITERATURE SURVEY

Before continuing with the discussion of specific techniques, two miscellaneous electrokinetic phenomena will be pointed out. The first, the Pallman effect,⁽⁸⁾ qualitatively explains the difference in pH between the supernate and the slurry, the second, the electro-viscous effect, gives a direct relationship between zeta potential and apparent viscosity of suspensions.

Pallman Effect

This effect is very succinctly discussed in Kryst,⁽⁹⁾ pp. 184-187.

"A simple experiment shows that two different results of the pH determination are possible. If a sol or suspension is in equilibrium with a particle-free solution (by dialysis or sedimentation) then a pH determination may be done in four different ways. The hydrogen electrode may be situated in the suspension or in the equilibrium liquid. The salt bridge also may be brought into contact with either of two systems.

The place of the hydrogen (or other reversible) electrode is without influence on the potential measured. This is necessarily so. For if two hydrogen electrodes in contact with the sol and the equilibrium solution would show a potential difference, work might be gained from a system in thermodynamic equilibrium, which is contrary to the Second Law.

The place of the salt bridge does make a difference, however. Usually the electrode connected to the salt bridge shows a lower potential when the salt bridge is in contact with the suspension than when it is in contact with the equilibrium solution at least if the suspension is negatively charged. For a positive suspension the effect is in the reverse direction."

This effect is qualitatively explained by the difference in the potential between the particle surface and the equilibrium solution due to

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the existence of the double layer. Generally the salt bridge will not indicate the potential of the equilibrium solution, but a potential nearer to that of the particles.

Electroviscous Effect⁽⁹⁾

The viscosity of a suspension of particles may be increased if the particles are charged, especially when the electrolyte concentration is low. Qualitatively one explanation is that in a laminar field of flow, the outer parts of the double layer are sheared from the particle. As they tend to restore themselves by conduction, the dissipation of energy manifests itself as a viscosity increase. Another possible explanation of the electroviscous effect in hydrophilic materials is based on the swelling of particles under the influence of the electrical repulsion between the charges.

Smoluchowski⁽¹²⁾ has derived a commonly quoted equation for the electroviscous effect. However, Booth⁽¹³⁾ has reconsidered the whole question and has concluded that Smoluchowski's relation gives results that may be too large by a factor of 100. Since the results of Booth's calculations are partially presented as graphs the reader is referred to his paper for more details.

Experimentally, recent measurements⁽¹⁴⁾ have proved the existence of a large electroviscous effect, proportional to the second and higher powers of the concentration.

Conductance Measurements

The theoretical background of electrical conductivity of suspension is given in Krut,⁽⁹⁾ page 238. The construction of equipment to measure the electrical conductivity of suspensions should be relatively simple, even for operation at elevated temperatures.

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Electro-Osmosis (9)(11)

Electro-osmosis is the tangential movement of a liquid with respect to a solid wall as a result of an applied potential gradient. A schematic diagram of an arrangement suitable for observing electro-osmosis is shown in Figure 1. P represents a porous plug. When a potential difference is set up between the electrodes E_1 and E_2 , the liquid is driven through the plug. The flow of liquid can be measured by the displacement of the meniscus M, in the capillary tube. Conditions that must prevail for accurate measurements are:

1. For dilute solutions the direction and velocity of flow depend only upon the properties of the plug and of the solution. For concentrated solutions correction must be made for water transport by electrolysis which depends only on the constitution of the liquid and is independent of the plug material.
2. For pores large compared to thickness of double layer, electro-osmosis is essentially independent of particle and pore size.
3. Accurate results with plugs can be obtained only if surface conductance is negligible.
4. Reversible electrodes such as Ag-AgCl will often have to be used in order to avoid gas being developed at the electrodes.

Streaming Potential (9)(11)

When a liquid is forced through a porous plug by an external pressure, a potential difference (the streaming potential) can be measured between two electrodes on either side of the plug. Equipment is similar to that for measuring electro-osmosis, although in this case the liquid flow is much greater and the potential differences are smaller.

Conditions that must prevail for satisfactory measurement are:

1. The flow of liquid through the plug pores must be laminar.

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2. Radius of curvature of the pores of the plug must be much larger than the thickness of the double layer.

3. Surface conductance must be negligible.

Electrophoresis (9)(11)(15)(16)

Electrophoresis is the movement of the particles in suspension in an electric field. The movement of particles may be observed by either a moving boundary method or by direct observation with an ultra-microscope. Conditions to be met for accurate measurements include:

1. The double layer must be thin compared with the particle dimensions.
2. Surface conductance must be negligible.
3. This type of measurement gives questionable results due to so-called relaxation effects arising from the movement of the charge in the double layer in a direction opposite to the movement of the particle itself.
4. Movement of the particle is independent of its shape.

Migration Potential

The reverse effect of electrophoresis arises when small particles which are suspended in a liquid are caused to move by gravitation or by an ultrasonic or a centrifugal field. An electric field is generated in the direction of movement and a potential difference can be measured between two electrodes in the liquid. The experiments are quite difficult.

Electro-osmosis and streaming potential measurements have the advantage that they can be made on concentrated solid-liquid mixtures. In both types of measurement the material to be investigated is packed in the form of a plug between two electrodes. The measured zeta-potential is independent of the length and cross section of the pores (provided these dimensions are greater than the thickness of the double layer) so that the packing of the plug or diaphragm is not critical.

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DISCUSSION

Electrophoresis measurement appears to be rather simple at room temperature. Although there appears to be complicating factors in the interpretation of the measurements, nevertheless the results would be comparable and would give useful information.

Measurements of electro-osmosis and streaming potential appear to be possible at elevated temperatures as well as at room temperature. Streaming potential measurements appear to be mechanically easier at elevated temperatures than electro-osmosis measurements, although this must be balanced against the lower potential developed in streaming potential measurements.

RECOMMENDATIONS

In order to provide a fundamental understanding of the action of electrolytes upon the physical properties of thorium-oxide slurries, a study of the zeta-potential (and other related phenomena) of thorium oxide should be made. This study should include the effect of different species and quantities of electrolytes and adsorbed hydrous oxides (e.g. corrosion-erosion products). Further, the possibility of extending these studies to elevated temperatures should be evaluated and if possible these measurements should be made.

The particular method that appears most useful for both high and low temperature studies is the streaming potential. The most difficult problem in the streaming potential measurement is the behavior of the electrodes at elevated temperatures. However M. H. Lietzke has been working on this problem⁽¹⁷⁾ for some time and could provide much assistance. The apparatus used would be similar to that shown in Figure 1 except that suitable

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arrangements would be made to cause a flow of liquid back and forth through the plug.

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P = Porous plug of material being
studied (i.e., ThO_2)
 E_1, E_2 = Electrodes
C = Capillary
M = Meniscus

Fig. 1 APPARATUS FOR OBSERVING ELECTRO-OSMOSIS

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