Study on water layer effect for paste performance and its plastic properties

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Abstract

Water layer has been known as an important element for battery paste performance, from the literature study and simple experiment, this paper gives evidence that water layer thickness for hydrosetting process to be important part for driving the crystallization process to the proper final result. Beside influence of paste performance, water layer also influence to paste plastic properties, only one property investigate in this paper related with correlation between water layer thickness with its compressive strength.
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1. Introduction

Why water layer to be important part of paste performance and its plastic properties?

If we look a model of double layer theory, that is water dipole model, the potential drop across the metal solution interface is interpreted only on the basis of a charge distribution across the interface and analogies are drawn between electrostatic capacitors and the double layer.
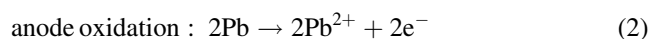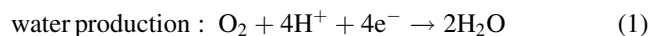
For example, let us suppose that we have a solid–solution interface, and there is no charge in the solid itself. The solution is one of sulfuric acid in the water and suppose the water molecule looks like that shown in Fig. 1; that is, it has a nonzero electric dipole moment or in other words, separation of charge within the molecule itself, now even in this simple case, the oxygen and the hydrogen may have different tendency to be close to the solid surface, and the water molecules may have orient themselves at the surface.

The strongly oriented water molecules important in consideration of adsorption of molecules on electrodes. It is a subject that is direct bearing on electrochemical energy conversion. This behavior may be rationalized using the water dipole model of the double layer as discussed above. Water 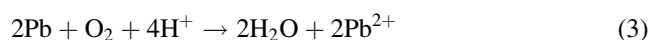molecules are adsorbed on the surface and discourage access of organic molecules to adsorption sites over most range of potential, water molecules are bounded to the electrode at least partly by electrostatic forces that are directly to the charge on the electrode. When this charge approach zero, the water molecules are held relatively poorly to the surface and oxygen molecules can replace them to adsorb on the electrode, oppositely if the water molecules are held strongly to the surface, the result is oxygen molecules repelled and decrease in coverage. In addition, it has been shown that it is necessary to take into consideration chemibonding between these species and the electrode.

1.1. Corrosion process

Anodic reaction is the main reaction for corrosion, but, many cathodic reaction must be considered due to cathodic reaction always together with anodic reaction. The main cathodic and anodic reaction in acid environment are: water production (1) and anode oxidation (2):

$$\text{water production}: \quad O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \tag{1}$$

$$\text{anode oxidation}: \quad 2Pb \rightarrow 2Pb^{2+} + 2e^- \tag{2}$$

Overall reaction:

$$2Pb + O_2 + 4H^+ \rightarrow 2H_2O + 2Pb^{2+} \tag{3}$$

In acid medium:

$$Pb^{2+} + 2H_2O \rightarrow PbO + 2H^+ \tag{4}$$

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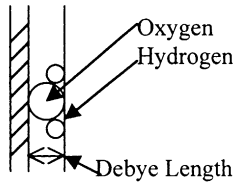[1] Tel.: +62-31-5946240/5924448; fax: +62-31-5999282.

Fig. 1. Double layer.

From the above set of equations, it is clear that water plays important role of the lead oxidation due to it act as a catalyst for reaction of oxygen and lead on the surface.

1.1.1. Transport phenomena

Suppose a crystal growth rate limited by mass transfer processes. From mathematical modeling the crystal growth rate equation could reduce to

$$R = \frac{DC_{BE}S_B}{\delta} \tag{5}$$

where R is the crystal growth rate, D the diffusion coefficient, C_{BE} the equilibrium concentration, S_B the supersaturation, δ the film thickness. Eq. (5) is an explanation of water layer effect to crystal growth rate.

Beside the above effect there is another effect of water. Let see the Eqs. (1)–(4). There is external diffusion effect on heterogeneous reaction between oxygen and hydrogen ion from acid solution and generate water. Oxygen move from air through plate surface and during its movement, oxygen react with hydrogen ion from sulfuric acid solution and PbO formation. For crystal growth rate there are three crystallization occur: PbO, and 3PbO-PbSO$_4$·H$_2$O (tribasic sulfate) and 4PbO-PbSO$_4$·H$_2$O (tetrabasic sulfate) formation and most of them are sphere, and cubes. Experimental evidence indicates that k_c may be reasonable well correlated by dimensionless equation

$$N_{Sh} = 2 + 0.6 \frac{D^{-2/3}}{v^{1/6}} \frac{U^{1/2}}{d_p^{1/2}} \tag{6}$$

This result, often called the Frossling equation, N_{Sh} is the Sherwood number and equal with

$$N_{Sh} = \frac{k_c d_p}{D_{AB}} \tag{7}$$

where k_c = mass transfer coefficient between crystal and water, d_p = particle diameter, D_{AB} = diffusion coefficient of water–crystal. When Eqs. (6) and (7) combined result

$$\frac{k_c d_p}{D_{AB}} = 2 + 0.6 \frac{D_{AB}^{2/3}}{v^{1/6}} \frac{U^{1/2}}{d_p^{1/2}} \tag{8}$$

and

$$\frac{k_c}{D_{AB}} = \delta \tag{9}$$

combine Eqs. (8) and (9) gives

$$\frac{d_p}{\delta} = 2 + 0.6 \frac{D_{AB}^{2/3}}{v^{1/6}} \frac{U^{1/2}}{d_p^{1/2}} \quad \text{or} \quad \sqrt{d_p} - \frac{\sqrt{d_p}}{\delta} - 2\sqrt{0.6}$$

$$= 0.6 \frac{D_{AB}^{2/3}}{v^{1/6}} U^{1/2} \tag{10}$$

In the above equation there is correlation between crystal diameter and mass transfer coefficient (k_c). From mass transfer theory there is correlation between diffusion coefficient and mass transfer coefficient with the following equation:

$$k_c = \frac{D_{AB}}{\delta} \tag{11}$$

where k_c = mass transfer coefficient, D_{AB} = diffusion coefficient of water–crystal, δ = water layer thickness and change k_c with D_{AB} for Eq. (6), it can obtain correlation between δ and crystal diameter with the following equation:

$$\delta = \frac{D_{AB}^{1/3} \leftrightarrow d_p^{1/2} \leftrightarrow v^{1/6}}{0.6 \leftrightarrow U^{1/2}} \tag{12}$$

Because U is relative velocity between water layer and solute sulfate and kinematic viscosity (v) may negligible, the Eq. (12) can reduce to

$$\delta = \frac{D_{AB}^{1/3} \times d_p^{1/2}}{0.6} \tag{13}$$

while D_{AB} is a diffusion coefficient between water and tribasic sulfate. Eq. (13) is an explanation of water layer correlation to crystal size.

Formation of tribasic sulfate crystal influenced by water layer. This phenomena can be explained by chemisorption equilibrium and kinetics. To enhance the hypothesis, an design of experiment has made. Through this experiment we wish to get more information related with adsorption type in the mixing process, mass transfer coefficient when sulfuric acid solution added into lead dust, and the optimum water layer thickness for optimum oxidation and recrystallization.

The step of experiment is:

1. Prepare the sulfuric acid with certain concentration (sulfuric acid concentration should similar with mixing process).
2. Weighing the lead dust in comparison as actual condition in the plant to get similar result with actual plant.
3. Mix the composition in the reactor with length of time as same as possible with operating condition.
4. At the end of mixing do analysis for them for each chemical composition: lead oxide; tribasic sulfate; lead sulfate; free lead and sulfuric acid residue.
5. Do again the steps 1–4 for different concentration of sulfuric acid.
6. From the experiment, plot a graphic between amount of sulfuric acid absorbed and sulfuric acid concentration.
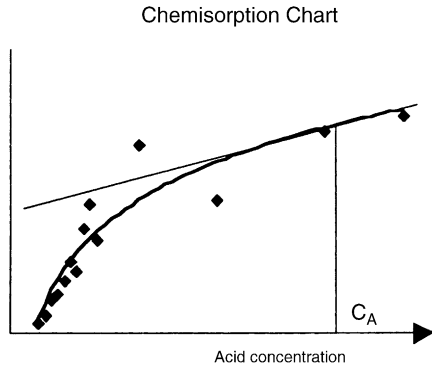
Chemisorption Chart

Fig. 2. Chemisorption.

Let's see Fig. 2. From the graphic, adsorption type and optimum acid concentration would be determined (see the vertical line indicate the optimum concentration of sulfuric acid).

From the graphic, obviously can be seen that the adsorption type is a chemisorption and a chemisorption need only one oxygen monomolecular of water layer thickness as a catalyst of lead oxidation and acid adsorption.

After we determine optimum water layer thickness, we should determine the optimum mass transfer coefficient, this experiment useful for determination of crystal growth rate and diffusion coefficient. Diffusion coefficient is useful to us because that parameter indicate the effectiveness of recrystallization process.

The step of the experiment is:

1. Prepare the sulfuric acid with certain concentration (sulfuric acid concentration should similar with mixing process).
2. Weighing the lead dust in comparison as actual condition in the plant to get similar result with actual plant.
3. Mix the composition in the reactor with length of time as same as possible with operating condition.
4. While mixing process running, take sample with certain time interval and do analysis for them for each chemical composition: lead oxide; tribasic sulfate; lead sulfate; free lead and sulfuric acid residue.
5. From the experiment, plot a graphic between amount of sulfuric acid absorbed and sampling time (see Fig. 3).
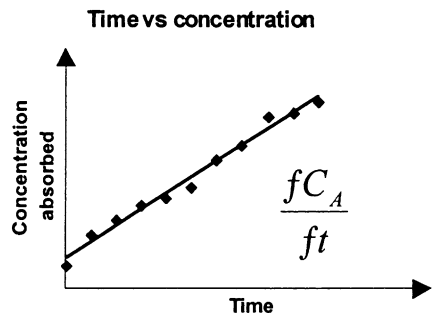
Time vs concentration

Fig. 3. Mass transfer coefficient determination.

Combine the optimum concentration of sulfuric acid from Fig. 2 with slope of Fig. 3 gives optimum mass transfer coefficient. From mass transfer coefficient can be determined the diffusion coefficient and water layer thickness with the equation below

$$E = f \frac{D\theta}{a^3} \tag{14}$$

E is the unreacted fraction of lead dust, D the diffusion coefficient, θ the optimum mixing time, a the particle diameter

$$\delta = \frac{k_c}{D} \tag{15}$$

δ is the water layer thickness, k_c the mass transfer coefficient, D the diffusion coefficient.

The main component of unformed paste is tribasic sulfate ($3PbO \cdot PbSO_4 \cdot H_2O$). There is an adsorption phenomena, that is $3PbO \cdot PbSO_4$ and H_2O. In this structure both of PbO and $PbSO_4$ bonded to H_2O. This phenomena can be explained by the following chemical reaction:

$$3PbO + PbSO_4 + H_2O \rightarrow 3PbO\text{-}PbSO_4 \cdot H_2O + \Delta H_{ads}$$
$$= -12,745 \text{ kJ/mol}$$
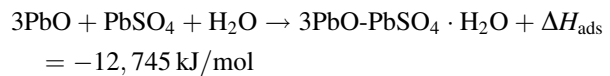
From the above equation heat of adsorption = 127,45 kJ/mol, that is value lie on chemisorption area, so this condition match with experimental result. For chemisorption, the absorption type is a type 1 in the Langmuir law and absorption takes place in monolayer. Monolayer calculated by considering the area S and volume V occupied by one mole of liquid water if it were spread over a surface to the depth of one molecular layer with the following equation:

$$\tau = \delta = \frac{V}{S} \tag{16}$$

Combine Eqs. (10) and (11) gives

$$\frac{V}{S} = \frac{D_{AB}^{1/3} \leftrightarrow d_p^{1/2}}{0.6} \tag{17}$$

2. Paste plastic properties

Paste plastic properties determined by its compressive strength. Considering the relation between water permeability and compressive strength of the paste and between gas permeability and strength, relation between diffusion coefficient and concrete strength should have the general form

$$D = \text{constant} \leftrightarrow \frac{1}{f_{cp}} \tag{18}$$

combine Eqs. (12) and (18) gives

$$0.6 \leftrightarrow \delta \leftrightarrow d_p^{1/2} = \text{constant} \leftrightarrow \frac{1}{f_{cp}} \tag{19}$$
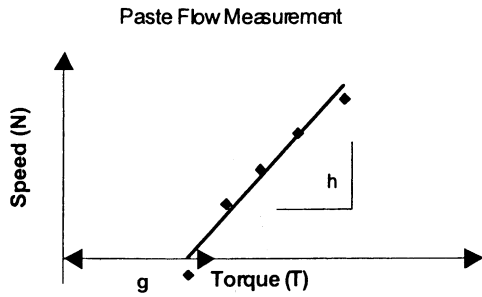
Paste Flow Measurement

Fig. 4. Paste plastic properties determination.

By an experiment, it can made a characteristic curve of the paste processing with the procedure below:

1. Prepare the equipment of experiment with procedure:
   ○ Connect the electric motor shaft of mixer with ampere–volt–ohm meter.
   ○ Fill mixer with lead and water.
   ○ Record the first ampere, and volt which can be from the apparatus.
   ○ Record the speed of the mixer impeller.
2. Do the experiment above with different speed of impeller.
3. With these result plot the graphic speed of impeller versus torque.

Torque can be calculated with relation that amperes proportional with power per unit time, from the above procedure, a graphic can be obtained like shown in Fig. 4.

In Fig. 4, g is an measure of yield value and h of plastic viscosity. From the plastic properties determination, we can adjust our paste production process suitable with our pasting machine, and as quality control of our pasting quality because with that result we can make sure that our process has already work consistently and information about the paste has already mix smoothly.

2.1. Hydrogen brittle

It has been known that hydrogen could be adsorbed when it traps while solidification process in the hydrosetting process occur.

The main characteristic of hydrogen brittle is:

1. Its sensitivity to rate of tension.
2. Dependability to temperature.
3. Susceptibility for deny the cleavage.

Hydrogen brittle has triggered by low rate of tension. This effect shows that hydrogen must inside the paste grain and must has high mobility with the result that brittle appear to polycrystal aggregate.

The common concept that had been accepted is the hydrogen monoatomic to precipitate inside the micropore or fissure as hydrogen molecule, and when pressure become larger than before, at finally facture happen.

According to Troiano, he has proposed that the critical factor is hydrogen aggregation, under working stress to the
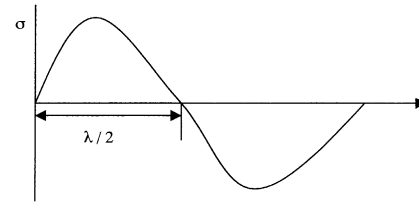

Fig. 5. Characteristic of fracture.

area of by triaxial stress near of edge of fissure, if hydrogen critical concentration has reached, the result are many new fissure formed and to be one with main fissure.

2.2. Griffith microfissure criteria

Usually material will be crack if working stress applied on the material has reach below theoretical facture stress. This stress depend on distance of two atoms and describe as a sinusoidal curve as in Fig. 5.

Fig. 5 explained that working stress (σ) is a function of u (deviation from equilibrium distance b) then the equation of Hooke is

$$\sigma = \sigma_t \sin \frac{2\pi u}{\lambda} U \sigma_t \frac{2\pi u}{\lambda} \tag{20}$$

where σ_t is a function of time (t).

For separation two atoms, it needed the surface energy γ and

$$2\gamma = \int_0^{\lambda/2} \sigma_t \sin \frac{2\pi u}{\lambda} \, du = \frac{\lambda \sigma_t}{2\pi} \tag{21}$$

with the result that theoretical stretch force is

$$\sigma_t = \sqrt{\frac{E\gamma}{b}} \tag{22}$$

This equation is called Griffith equation. If crack fissure because of dislocation mechanism, Griffith equation must be reformulate and include the dislocation number, n which is form the fissure and the equation become

$$\sigma - \frac{c\sigma}{E} = \gamma \tag{23}$$

where the multiplication between $2b$ and σ/E is a maximum movement between fissure surface and the Eq. (23) become

$$\sigma n a = 2\gamma \tag{24}$$

and

$$\gamma = \gamma_p + \gamma \tag{25}$$

From the above equation, water layer effect lies on stress of σ. Now what is the relationship?

2.3. Facture mechanism

The main characteristic of facture is immediately release of dislocation when crushing happen. There are three factors that influence fracture mechanism. These are lattice friction σ_i, dislocation locking k_y and grain size d because each time
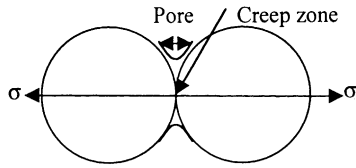
Fig. 6. Adhesive of two grain.

increasing of σ_i, k_y and decreasing of grain size would be increase the crush stress.

2.4. Pore analysis by adsorption

Adsorption studies leading to measurements of pore size generally make use of the Kelvin equation

$$\ln \frac{P}{P_0} = \frac{2\gamma V}{rRT} \cos \theta \qquad (26)$$

where P is the equilibrium vapor pressure of the liquid contained in a narrow pore of radius r and P_0 the equilibrium pressure the same liquid exhibiting a plane surface or in simplified model the equation gives

$$\Delta P = \frac{2\gamma}{r} \qquad (27)$$

If Eq. (27) compared than Eq. (24), there is a correlation that $na = r$ = water layer thickness.

Let us see Figs. 6–9. From these figures, which can simplified by the Fig. 7a. L is a length of facture. When this length multiplied with strain (σ/E) gives the maximum movement between fissure surface. This movement depend on number of dislocation and the above equation can derived into

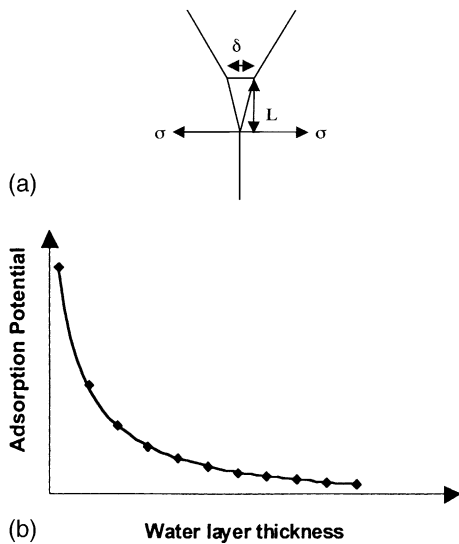$$\sigma - \frac{\sigma}{E} = \gamma \qquad (28)$$

or

$$\sigma na = 2\gamma \qquad (24)$$

(a)

(b)

Fig. 7. Facture of Grain boundary (a). Water layer–adsorption potential correlation (b).
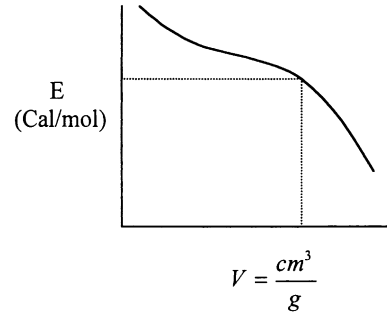

$$V = \frac{cm^3}{g}$$
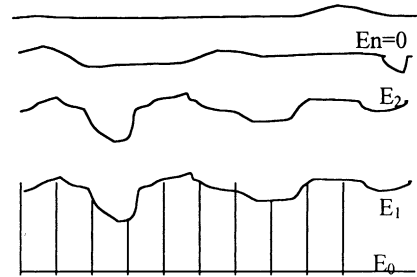
Fig. 8. Characteristic curve.

Fig. 9. Polany's potential planes.

So, in the above surface, water layer correlation shown by

$$\delta = \frac{\gamma}{\sigma} \leftrightarrow \frac{E}{\sigma} \qquad (29)$$

where δ is water layer thickness. E is isothermal work and σ is axial stress of the grain.

2.5. Adsorption potential

Beside give influence to axial stress, water layer also gives influence to adsorption potential. The potential theory assert that the adsorption potential, when the adsorbate is in the liquid state, is given by

$$E = RT \ln \frac{P_0}{P} \qquad (30)$$

E is the isothermal work required to compress the vapor from its equilibrium pressure P to the saturated vapor P_0 of the liquid in the adsorption volume.

The adsorption volume is considered only liquid. One can write

$$V = \frac{W}{\rho} \qquad (31)$$

From the experimental isotherm, can be derived

$$V = FE \qquad (32)$$

The curve can shown in Fig. 8 or visually we can describe the graphic into physical drawing given in Fig. 9.

From Polany's potential planes, $E_n = 0$ that means the thicker the layer, the higher energy to compress the vapor from its equilibrium pressure P to the saturated pressure P_0 of the liquid in the adsorption volume.

From adsorption potential, it can correlated with water layer thickness so, from this correlation, once more we have to concern about water layer effect to paste performance. The correlation can derived with the correlation

$$\frac{2\gamma V}{r} = E \tag{33}$$

Where V is the water volume remain in the paste, r the pore diameter, γ the surface tension, E the adsorption potential.

From the above equation we can plot into Fig. 7b.

3. Conclusion

1. Water layer is one of important element for paste properties due to its impact to:
   (a) Tribasic sulfate formation.
   (b) Crystal growth rate.

2. Water layer thickness should only monolayer of one water molecule related to maximize the crystal growth rate and hydrate adsorption to tribasic sulfate formation.

3. To determine the paste plastic property it is necessary for finding the correlation between water layer thickness and paste compressive strength as the optimum strength.

4. The important of water component is hydrogen and the main characteristic of hydrogen brittle is:
   (1) Its sensitivity to rate of tension.
   (2) Dependability to temperature.
   (3) Susceptibility for deny the cleavage.

5. Water layer gives influence to facture formation and adsorption potential which is important for oxidation and water and acid adsorption.