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*Effect of Operating Parameters
and Chemical Additives on Crystal Habit
and Specific Cake Resistance
of Zinc Hydroxide Precipitates*

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Jennifer Louise Alwin

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NOMENCLATURE

θ	$\equiv$	time, s
w	$\equiv$	dry weight of cake per unit filtrate volume, kg/m ³
A	$\equiv$	area, m ²
$V(\theta)$	$\equiv$	filtrate volume collected at time θ , m ³
μ	$\equiv$	filtrate viscosity, Ns/m ³ , ionic strength of solution
P	$\equiv$	differential pressure, N/m ²
α	$\equiv$	specific cake resistance, m/kg
r	$\equiv$	resistance of filter media, m ⁻¹
K_i	$\equiv$	equilibrium constant of species i
K_i^{sp}	$\equiv$	solubility product constant of species i
N_i	$\equiv$	number of moles
n_i	$\equiv$	number of moles
$[i]$	$\equiv$	concentration of species i , mol/L
W	$\equiv$	rate of energy transfer, watts
s	$\equiv$	specific gravity
d	$\equiv$	depth at which air is released into tank, m
N_{Re}	$\equiv$	Reynolds number
Φ	$\equiv$	function used to determine power input
D	$\equiv$	impeller diameter, m

N	$\equiv$	impeller speed, rev/sec
g	$\equiv$	gravitational constant, m/s^2
ρ	$\equiv$	density of fluid, kg/m^3
ρ_s	$\equiv$	density of solid, kg/m^3
a	$\equiv$	constant used in evaluation of power input
b	$\equiv$	constant used in evaluation of power input
c	$\equiv$	concentration of ion, mol/L
z	$\equiv$	charge of individual ion
C	$\equiv$	volume fraction solids
C_w	$\equiv$	mass fraction solids
k	$\equiv$	permeability, m

EFFECT OF OPERATING PARAMETERS AND CHEMICAL ADDITIVES
ON CRYSTAL HABIT AND SPECIFIC CAKE RESISTANCE OF
ZINC HYDROXIDE PRECIPITATES

BY

JENNIFER LOUISE ALWIN

ABSTRACT

The effect of process parameters and chemical additives on the specific cake resistance of zinc hydroxide precipitates was investigated. The ability of a slurry to be filtered is dependent upon the particle habit of the solid and the particle habit is influenced by certain process variables. The process variables studied include neutralization temperature, agitation type, and alkalinity source used for neutralization. Several commercially available chemical additives advertised to aid in solid/liquid separation were also examined in conjunction with hydroxide precipitation.

A statistical analysis revealed that the neutralization temperature and the source of alkalinity were statistically significant in influencing the specific cake resistance of zinc hydroxide precipitates in this study. The type of agitation did not significantly effect the specific cake resistance of zinc hydroxide precipitates. The use of chemical additives in conjunction with hydroxide precipitation had a favorable effect on the filterability. The

morphology of the hydroxide precipitates was analyzed using scanning electron microscopy.

1. INTRODUCTION

Many chemical processes produce acidic waste streams which contain dissolved metals in solution. The most common method for removal of such metals from solution is chemical precipitation (Tunay and Kahdasli 1994, Baltpurvins et al. 1997). Precipitation is rapid crystallization caused by the addition of reagents which lower the solubility of the metals in solution to form insoluble particles which can be removed by filtration. Hydroxide precipitation, or precipitation by pH adjustment, requires the use of hydroxide to raise the pH of the solution, and thus lower the solubility of the metals in solution.

Hydroxide precipitation is used widely because of its advantages which include performance in meeting effluent discharge requirements, ease of operation, and relative cost of operation (Tunay and Kahdasli 1994). There are also several disadvantages to the use of hydroxide precipitation. Complexed metals cannot be efficiently removed from solution using hydroxide precipitation (Tunay and Kahdasli 1994). Metal hydroxide precipitates are amphoteric, thus a change in pH results in increased solubility for the hydroxide precipitate (ETUS, Inc. 1996). Additionally, metal hydroxides are hydrophilic and result in slurries that have been found difficult to dewater and filter.

1.1 Purpose of Research

Hydroxide precipitation has been effective in the separation of radioactive metals, such as plutonium, from spent process acid solutions. The long-term goal of this research is an attempt to model plutonium hydroxide precipitation using a less hazardous, non-radioactive surrogate system. The surrogate system chosen was zinc chloride dissolved in hydrochloric acid. This portion of the research encompasses a fundamental study of process parameters which influence the particle size and morphology of the hydroxide precipitates. Desired outcomes are the identification of process conditions for this chemistry that lead to improved filterability of the hydroxide slurry, and a predictive model for the composition and specific cake resistance of solid precipitates in these systems.

Many independent variables are known to influence particle size and morphology. These variables include; nature of the solvent, pH of the solution, presence of impurities and additives, degree of supersaturation, neutralization temperature, agitation, aging, production rate, residence time, seeding, slurry density, and others (Mullin 1972, Genck 1989, Chen, Yai and Shih 1992). The focus of this research is to investigate the effects of neutralization temperature, agitation type, alkalinity source, and chemical additives on the specific cake resistance of zinc hydroxide precipitates.

1.2 Reactions of Hydroxides

The complexation reactions which take place between zinc chloride and potassium hydroxide or magnesium hydroxide have been identified in the literature (Smith and Martell 1989). The Zn^{2+} cation forms strong complexes with the Cl^- anion (Tossel 1991). A method for studying the various reactions, including complexation reactions, is by the use of chemical equilibrium diagrams (Tossel 1991, Cadena and Midkiff 1994, Baltpurvins, Burns and Lawrence 1996) which provide species equilibrium concentrations as a function of pH. The construction of chemical equilibrium diagrams requires the simultaneous solution of the total mole balance, independent species mole balances and the proton balance; while considering the relative equilibrium concentration and species solubilities. The equations are combined to determine species concentration as a function of hydrogen ion concentration. The number of equations to be solved equals the number of species in the solution.

Identified complexation equilibria for the zinc chloride system and magnesium hydroxide system are (Smith and Martell 1989):

The equilibrium constants are designated, K_i and are defined and quantified in Table 1 (Smith and Martell 1989).

Material balances for the species Zn^{2+} , Cl^- , and Mg^{2+} are:

$$\begin{aligned} N_{Zn} = & n_{ZnCl}^+ + n_{Zn}^{2+} + n_{ZnCl_3}^- + n_{ZnCl_2} + n_{ZnCl_4}^{2-} + n_{Zn(OH)}^+ + n_{Zn(OH)_2} \\ & + n_{Zn(OH)_3}^- + n_{Zn(OH)_4}^{2+} + n_{Zn_2(OH)_3}^+ \end{aligned} \quad (1.16)$$

$$N_{Cl} = n_{Cl}^- + n_{ZnCl_2} + n_{ZnCl}^+ + n_{ZnCl_4}^{2-} + n_{ZnCl_3}^- + n_{MgCl}^+ \quad (1.17)$$

$$N_{Mg} = n_{MgCl}^+ + n_{Mg_4(OH)_4}^{4+} + n_{Mg(OH)_2} + n_{Mg(OH)}^+ \quad (1.18)$$

Table 1. Equilibrium Constants for Zn^{2+} , Mg^{2+} , Cl^- , OH^- System

Species, i	K_i or K_i^{sp}	$\log K_i$ or $\log K_i^{\text{sp}}$
ZnCl^+	$[\text{ZnCl}^+]/[\text{Zn}^{2+}][\text{Cl}^-]$	0.43
ZnCl_2	$[\text{ZnCl}_2]/[\text{Zn}^{2+}][\text{Cl}^-]^2$	0.61
ZnCl_3^-	$[\text{ZnCl}_3^-]/[\text{Zn}^{2+}][\text{Cl}^-]^3$	0.50
ZnCl_4^{2-}	$[\text{ZnCl}_4^{2-}]/[\text{ZnCl}_3^-][\text{Cl}^-]$	0.20
$\text{Zn}_2(\text{OH})_3\text{Cl}$	$[\text{Zn}^{2+}]^2[\text{OH}^-]^3[\text{Cl}^-]$	-13.40
$\text{Zn}(\text{OH})_2(\text{s})$	$[\text{Zn}^{2+}][\text{OH}^-]^2$	-15.52
$\text{Zn}(\text{OH})^+$	$[\text{Zn}(\text{OH})^+]/[\text{Zn}^{2+}][\text{OH}^-]$	5.00
$\text{Zn}(\text{OH})_2$	$[\text{Zn}(\text{OH})_2]/[\text{Zn}^{2+}][\text{OH}^-]^2$	11.11
$\text{Zn}(\text{OH})_3^-$	$[\text{Zn}(\text{OH})_3^-]/[\text{Zn}^{2+}][\text{OH}^-]^3$	13.60
$\text{Zn}(\text{OH})_4^{2-}$	$[\text{Zn}(\text{OH})_4^{2-}]/[\text{Zn}^{2+}][\text{OH}^-]^4$	14.80
$\text{Zn}_2(\text{OH})^{3+}$	$[\text{Zn}_2(\text{OH})^{3+}]/[\text{Zn}^{2+}]^2[\text{OH}^-]$	5.00
MgCl^+	$[\text{MgCl}^+]/[\text{Mg}^{2+}][\text{Cl}^-]$	-1.00
$\text{Mg}(\text{OH})_2(\text{s})$	$[\text{Mg}^{2+}][\text{OH}^-]^2$	-11.15
$\text{Mg}(\text{OH})^+$	$[\text{Mg}(\text{OH})^+]/[\text{Mg}^{2+}][\text{OH}^-]$	2.58
$\text{Mg}_4(\text{OH})_4^{4+}$	$[\text{Mg}_4(\text{OH})_4^{4+}]/[\text{Mg}^{2+}][\text{OH}^-]$	16.30

Electroneutrality is maintained using a proton balance:

$$[\text{H}^+] + 2[\text{Zn}^+] + 2[\text{Mg}^+] = [\text{OH}^-] + [\text{Cl}^-] \quad (1.19)$$

Simultaneous solution of the above equations yields equilibrium concentration of each species versus pH diagrams for the system. The

equilibrium concentration diagram for the zinc chloride/magnesium hydroxide system is shown in Figure 1.

Figure 1. Equilibrium Concentration Diagram for Zinc Chloride/Magnesium Hydroxide System

Identified complexation equilibria for the zinc chloride and potassium hydroxide system are (Smith and Martell 1989):

The equilibrium constants are designated, K_i and are defined and quantified in Table 2 (Smith and Martell 1989).

Material balances for the species Zn^{2+} , Cl^- , and Mg^{2+} are:

$$\begin{aligned} N_{\text{Zn}} = & n_{\text{ZnCl}^+} + n_{\text{Zn}^{2+}} + n_{\text{ZnCl}_3^-} + n_{\text{ZnCl}_2} + n_{\text{ZnCl}_4^{2-}} + n_{\text{Zn}(\text{OH})^+} + \\ & n_{\text{Zn}(\text{OH})_2} + n_{\text{Zn}(\text{OH})_3^-} + n_{\text{Zn}(\text{OH})_4^{2-}} + n_{\text{Zn}_2(\text{OH})_3^+} \end{aligned} \quad (1.31)$$

$$N_{\text{Cl}} = n_{\text{Cl}^-} + n_{\text{ZnCl}_2} + n_{\text{ZnCl}^+} + n_{\text{ZnCl}_4^{2-}} + n_{\text{ZnCl}_3^-} + n_{\text{KCl}} \quad (1.32)$$

$$N_{\text{K}} = n_{\text{KCl}} + n_{\text{K}^+} \quad (1.33)$$

Electroneutrality is maintained using a proton balance:

$$[\text{H}^+] + 2[\text{Zn}^+] + [\text{K}^+] = [\text{OH}^-] + [\text{Cl}^-] \quad (1.34)$$

Table 2. Equilibrium Constants for Zn^{2+} , K^+ , Cl^- , OH^- System

Species, i	K_i or K_i^{sp}	$\log K_i$ or $\log K_i^{\text{sp}}$
ZnCl^+	$[\text{ZnCl}^+]/[\text{Zn}^{2+}][\text{Cl}^-]$	0.43
ZnCl_2	$[\text{ZnCl}_2]/[\text{ZnCl}^+][\text{Cl}^-]$	0.61
ZnCl_3^-	$[\text{ZnCl}_3^-]/[\text{ZnCl}_2][\text{Cl}^-]$	0.50
ZnCl_4^{2-}	$[\text{ZnCl}_4^{2-}]/[\text{ZnCl}_3^-][\text{Cl}^-]$	0.20
$\text{Zn}_2(\text{OH})_3\text{Cl}$	$[\text{Zn}^{2+}]^2[\text{OH}^-]^3[\text{Cl}^-]$	-13.40
$\text{Zn}(\text{OH})_2(\text{s})$	$[\text{Zn}^{2+}][\text{OH}^-]^2$	-17.10
$\text{Zn}(\text{OH})^+$	$[\text{Zn}(\text{OH})^+]/[\text{Zn}^{2+}][\text{OH}^-]$	5.00
$\text{Zn}(\text{OH})_2$	$[\text{Zn}(\text{OH})_2]/[\text{Zn}^{2+}][\text{OH}^-]^2$	11.11
$\text{Zn}(\text{OH})_3^-$	$[\text{Zn}(\text{OH})_3^-]/[\text{Zn}^{2+}][\text{OH}^-]^3$	13.60
$\text{Zn}(\text{OH})_4^{2-}$	$[\text{Zn}(\text{OH})_4^{2-}]/[\text{Zn}^{2+}][\text{OH}^-]^4$	14.80
$\text{Zn}_2(\text{OH})_3^+$	$[\text{Zn}_2(\text{OH})_3^+]/[\text{Zn}^{2+}]^2[\text{OH}^-]$	5.00
KCl	$[\text{KCl}]/[\text{K}^+][\text{Cl}^-]$	-0.70

Simultaneous solution of the above equations yields equilibrium concentration of each species versus pH diagrams for the system. The equilibrium concentration diagram for the zinc chloride/potassium hydroxide system is shown in Figure 2.

The equilibrium expressions used for construction of the above equilibrium concentration diagrams were evaluated under the assumption that the molar activity and the molar concentration were equal. Equilibrium

Figure 2. Equilibrium Concentration Diagram for Zinc Chloride/Potassium Hydroxide System

constants are a function of the ionic strength of the solution. Ionic strength is defined by Equation 1.35 (Ringbom 1963).

$$\mu = \frac{1}{2} \sum cz^2 \quad (1.35)$$

where, c $\equiv$ concentration of individual ion, mol/L

z $\equiv$ charge of individual ion

At high ionic strength, the activity of an ion is equal to the product of the activity coefficient and the concentration. Equating the molar

concentration and the molar activity is done to provide an approximation of actual chemical conditions. The equilibrium concentration diagrams constructed are useful in determining favorable conditions for precipitation and allow visualization of approximate species concentration conditions at a glance, although this simplification will lead to differences from actual equilibrium conditions in strongly non-ideal solutions as studied in this experimental work.

1.3 Specific Cake Resistance

The standard engineering measure of the filterability of a slurry is the specific cake resistance (α) as described by Equation 1.36 for liquid flow through a *forming* cake during constant pressure filtration (Perry and Green 1997):

$$\frac{\theta A}{V} = \frac{\mu \alpha w}{2PA} V + \frac{\mu r}{P} \quad (1.36)$$

where, θ $\equiv$ time, s

w $\equiv$ mass of dry cake solids per unit filtrate volume, kg/m³

A $\equiv$ area, m²

$V(\theta)$ $\equiv$ filtrate volume collected at time θ , m³

μ $\equiv$ filtrate viscosity, Ns/m²

P $\equiv$ differential pressure, N/m²

α $\equiv$ specific cake resistance, m/kg

$r \equiv$ resistance of filter media, m^{-1}

The first term on the right hand side of Equation 1.36 is the resistance due to the formation of the cake while the second term on the right hand side of Equation 1.36 is the resistance due to the filter medium. Plotting experimental values of θ/V against V allows for calculation of the slope, $\mu\alpha w/2A^2P$, and the intercept, $\mu r/AP$. Using physical property data, the cross sectional area of the filtration apparatus and the slope and intercept of the θ/V line, the specific cake resistance, α , may be calculated. An example of the plot of the θ/V line is shown in Figure 3.

Figure 3. Typical Constant Pressure Filtration Plot to Determine Specific Cake Resistance and Filter Medium Resistance

Saranteas and Botsaris (1997) report simple guidelines to determine how values of specific cake resistance relate to ease of filterability:

<u>Specific Cake Resistance, m/kg</u>	<u>Filtration</u>
10^{10} - 10^{11}	easy
10^{11} - 10^{12}	moderate
10^{12} - 10^{13}	difficult
10^{13} - 10^{14}	very difficult

Filtration results are often given in terms of cake permeability, which characterizes the ease with which liquid flows through a porous medium (Rushton, Ward and Holdich 1996). The relationship between permeability and specific cake resistance is given in Equation 1.37.

$$\alpha = \frac{1}{kC\rho_s} \quad (1.37)$$

where, $k \equiv$ cake permeability, m^2

$C \equiv$ volume fraction of solids

$\rho_s \equiv$ solid density, kg/m^3

The volume fraction of solids, C , may be calculated using Equation 1.38.

$$C = \left(1 + \frac{(1 - C_w)}{C_w \rho} \rho_s \right)^{-1} \quad (1.38)$$

where, C_w $\equiv$ mass fraction of solids

ρ $\equiv$ liquid density, kg/m^3

1.4 Crystal Habit

Molecules, ions or atoms of every solid crystal are arranged in a structured lattice which results in smooth surfaces or faces that give the solid a characteristic shape. Although the size of the crystal faces may vary, the angle between faces remains constant. The *crystal habit* is the external crystalline shape resulting from variation in the growth rates of the crystal faces.

Under certain process conditions, one crystal face may grow faster or slower than others, leading to different habits. A large number of factors can affect the crystal habit of a solid, including the type of solvent, the pH of the solution, presence of impurities, crystallization temperature, and agitation (Mullin 1972).

The ability of a slurry to be filtered is influenced by the crystal habit of the solid. Certain crystal habits may result in undesirable solid properties that tend to induce poor flow characteristics. For effective filtration, the most favorable habits are usually cubic or prismatic, while the least favorable are typically plates or needles. As shown in Figure 4, the cubic and prismatic habits are compact and allow fluid flow between crystals. Due to the long, thin

nature of plates or needles, they can stack together and prohibit fluid flow or clog filter media.

Figure 4. Typical Crystal Habits

1.5 Effect of Process Parameters

1.5.1 Temperature

Temperature has a great deal of influence on the formation and growth of particles. Vian, Rodriguez and Guardiola (1983) report that increasing the precipitation temperature leads to solid products which are more crystalline and larger in size for precipitates obtained from zinc oxi-hydroxychloride suspensions. They also report that at lower temperatures there is an increase in the specific cake resistance. The existence of larger particles can be explained by slower growth rates of the particles due to increased solubility at higher temperatures. Increasing the operating temperature may lead to *diffusion-controlled conditions*, as opposed to *integration-controlled conditions*. Diffusion-controlled conditions produce better quality crystals since the molecules arriving at the site can be organized into the crystal structure. In contrast, integration controlled conditions lead to increased nucleation and

therefore more particles of smaller sizes (Dutt, Kameshuri and Subbarao 1998). During integration-controlled conditions, molecules arriving at the site cannot be organized into the crystal structure and many small crystals are formed by increased nucleation.

When precipitating at elevated temperatures, subsequent cooling can lead to particle growth since supersaturation, the driving force for both growth and birth, can be achieved by cooling (Genck 1989). Studies have been done to try to optimize the cooling rate to allow favorable crystal growth (Giulietti et al. 1996).

1.5.2 Agitation

Moussaouiti et al. (1997) found that mixing affects growth rates due to mass transfer, but does not appear to influence nucleation rates. Ideal mixing provides sufficient mass transfer to allow reaction, but does not cause secondary nucleation due to attrition of particles. In this study, comparison of mixing provided by mechanical agitation with mixing provided by air sparging into the reactor was attempted. Comparison of the two agitation types was accomplished by equating the rate of energy transfer. The rate of energy transfer for air agitation is (Lamont 1958):

$$W = 144PV \ln \frac{2.31 + sd}{2.31P} \quad (1.39)$$

Where, W = rate of energy transfer from air to vessel, Watts

P = absolute pressure at the top of the tank, N/m²

V = air volume rate, m³/s

s = specific gravity

d = depth at which air is released into the tank, m

The rate of energy transfer for mechanical agitation is obtained using Equation 1.40 (Rushton, Costich and Everett 1950) correlated with the Reynolds number, N_{Re} :

$$\Phi = \left(\frac{Pg}{\rho N^3 D^5} \right) \left(\frac{g}{N^2 D} \right)^{\left(\frac{a - \log N_{Re}}{b} \right)} \quad (1.40)$$

Where, Φ ≡ function used to determine power input

P ≡ pressure, N/m²

N ≡ impeller speed, rev/sec

D ≡ impeller diameter, m

g ≡ gravitational constant, m/s²

ρ ≡ density of fluid, kg/m³

a ≡ constant used in evaluation of exponent

b ≡ constant used in evaluation of exponent

The power from mechanical agitation is calculated using correlations available in the literature (Rushton, Costich and Everett 1950):

$$N_{Re} = \frac{D^2 N_p}{g} \quad (1.41)$$

1.5.3 Alkalinity Source

The alkalinity source used for the precipitation can have a significant effect on the precipitate and the precipitate morphology. For this study, potassium hydroxide (KOH) and magnesium hydroxide (Mg(OH)₂) were compared. These two alkalinity sources were chosen because they are used in the actual processing of nuclear materials.

Neutralization with potassium hydroxide can be considered a one-step process since it is a strong base and dissociates completely when added to the reaction vessel. Hydroxyl ions are numerous in the feed and thus react very quickly. The fast reaction of the potassium hydroxide with the acidic solution produces a precipitate that may be difficult to filter. Reaction kinetics are so fast that metal hydroxide precipitates are inter-dispersed with water and results in a slurry that is gelatinous and occupies considerable volume (Dow Chemical Company 1996).

The reaction mechanism of magnesium hydroxide differs markedly from potassium hydroxide since magnesium hydroxide is virtually insoluble in water. The dissolution of magnesium hydroxide in acid solutions occurs as the first step in the reaction. This heterogeneous mass transfer process effectively limits the availability of hydroxyl ions. Since magnesium hydroxide is a weak base, the final neutralized solution is buffered and the neutralization reaction occurs slowly as the pH increases, ultimately not exceeding pH 9.0. In contrast, the reaction with potassium hydroxide occurs quickly and even a slight excess of reagent can lead to very high pH values.

1.6 Effect of Chemical Additives

The presence of additives or impurities can have a significant influence on the resulting particle size and particle habit of a precipitate. Additives may be used in the feedstreams or as an after-treatment to influence the particle habit or size distribution (Genck 1990, Van Rosmalen and Bennema 1990, Kipp, Lacmann and Rolfs 1997).

Additives used in this study include precipitating agents, coagulants and flocculants obtained from ETUS, Inc. (Sanford, Florida). Precipitating agents may be applied after pH adjustment to cause precipitation of the metal complexes in solution and are used to break complexation rings and lower the solubility of metal hydroxides and to change the amphoteric nature of the metal

hydroxides (ETUS, Inc. 1996). The precipitating agents used in this study were THIO-RED (a polythiocarbonate compound), SP-PLUS (a blended reagent containing both organic and inorganic compounds), and CP-PLUS (a chelate breaker precipitant with a catalytic additive). The chemical additives used in this study are proprietary products and therefore exact chemical compositions are not available.

Hydroxide precipitation often results in the formation of colloidal particles that are electrically charged and typically less than 1 μm in size (Rushton, Ward and Holdich 1996). Due to charge repulsion and size, colloids tend to remain suspended in solution. It is, however, possible to destabilize colloidal suspensions by the addition of chemical additives and subsequently enhance settling and filtration.

Stabilization of colloids may be explained by the double layer theory (Rushton, Ward and Holdich 1996), in which an electrolytic solution containing ions of both positive and negative charge attract ions of opposing charge and repel ions of like charge. This results in a double layer of ions around the particle which produces both concentration and electrical potential gradients. Coagulants act to compress the double layer and reduce the surface charge repulsion. (Rushton, Ward and Holdich 1996).

Flocculants are long-chained polymers and are often added after coagulants to produce clusters of particles. They become adsorbed onto the surface of the particle (Rushton, Ward and Holdich 1996) and when other particles collide with the polymer covered particle, adsorption occurs and particle growth continues with the formation of “flocs.” It is critical to provide enough agitation so that the particles collide sufficiently, although high rates of shear may result in the breakage of the particles. M-25 coagulant/flocculant (a liquid polyquarternary amine coagulant with a cationic charge) and ANF-15 flocculant (a liquid organic flocculant with an anionic charge) from ETUS, Inc. were used in this study.

2. EXPERIMENTAL DESIGN

2.1 Process Parameter Effects

A statistical experimental design was used to determine effects among factors. A fractional factorial design of experiments was chosen and three independent variables (neutralization temperature, agitation type and alkalinity source) were chosen to create an effect on the statistical response variable (the specific cake resistance). The agitation type and the alkalinity source consisted of two levels each and the temperature was studied at four different levels. When using a fractional factorial experimental design, factors with four levels can be handled by recoding them into two factors of two levels each (Mason, Gunst and Hess 1989). A 2^{4-1} fractional factorial experiment with two replicates was used resulting in 16 experimental runs. Table 3 shows the factors and levels for the experimental design which was executed in random order to minimize experimental error and its impact on the analysis of variance.

2.2 Additive Effects

The effect of additives on specific cake resistance was determined through a dosage study. Experimental runs using three different additives at several dose levels were used to examine effects on precipitates obtained using potassium hydroxide and precipitates obtained from magnesium hydroxide.

The experimental runs are listed in Table 4 with larger dosages used for the slurries neutralized with magnesium hydroxide due to its buffering effect.

Table 3. Experimental Design for Process Parameter Study

Run Number	Temperature (°C)	Alkalinity Source	Agitation Type
8	10	KOH	Mechanical
7	10	Mg(OH) ₂	Air
6	25	KOH	Air
1	25	Mg(OH) ₂	Mechanical
4	50	KOH	Air
2	50	Mg(OH) ₂	Mechanical
5	70	KOH	Mechanical
3	70	Mg(OH) ₂	Air

Table 4. Experimental Runs for Additive Study

Run Number	Alkalinity Source	Precipitating Agent	Dose (wt %)
KCP1	KOH	CP-Plus	1%
KCP2	KOH	CP-Plus	2%
KCP4	KOH	CP-Plus	4%
KT1	KOH	THIO-RED	1%
KT2	KOH	THIO-RED	2%
KT4	KOH	THIO-RED	4%
KSP1	KOH	SP-Plus	1%
KSP2	KOH	SP-Plus	2%
KSP4	KOH	SP-Plus	4%
K	KOH	None	-
MT2	Mg(OH) ₂	THIO-RED	2%
MT4	Mg(OH) ₂	THIO-RED	4%
MT8	Mg(OH) ₂	THIO-RED	8%
MSP2	Mg(OH) ₂	SP-Plus	2%
MSP4	Mg(OH) ₂	SP-Plus	4%
MSP8	Mg(OH) ₂	SP-Plus	8%
MCP2	Mg(OH) ₂	CP-Plus	2%
MCP4	Mg(OH) ₂	CP-Plus	4%
MCP8	Mg(OH) ₂	CP-Plus	8%
M	Mg(OH) ₂	None	-

3. EXPERIMENTAL PROCEDURE

3.1 Hydroxide Precipitation

Neutralization was carried out in a glass Kimble/Kontes 1-liter jacketed reaction vessel with a discharge valve at the bottom of the reactor. The top of the reaction vessel contained four ports for instrumentation and addition of reagents as illustrated in Figure 5.

Figure 5. Experimental Apparatus

Ethylene glycol was circulated through the reaction vessel jacket using a Cole Parmer Programmable Temperature Controller Series Constant Temperature Circulating Bath, to maintain the temperature of the reaction. Reaction temperature was also maintained by adjusting the addition rate of hydroxide to the vessel.

Slurry pH was measured using a Fisher pH electrode with a built-in automatic temperature compensation (ATC) probe and a Cole-Parmer pH/ORP (oxidation/reduction potential) controller. The electrode was calibrated using buffer solution to maintain accurate pH readings.

The temperature of the reaction was measured using a type K thermocouple and an Omega Data Logger. To protect the thermocouple wire from corrosive attack, it was inserted into a glass tube containing silicon oil. The silicon oil was used to promote good heat transfer to the probe junction.

Mechanical mixing was provided with a 3-blade Teflon propeller controlled by a Servodyne Mixer Controller and Servodyne Mixer. Agitation speed was kept at 250 rpm for all reactions. Air agitation was provided by the use of a gas cylinder of compressed air and the flow rate of air into the vessel was maintained at $7.87 \times 10^{-5} \text{ m}^3/\text{s}$. The gas flowed into a 12.7 mm diameter air sparge and out a glass frit at the bottom of the reaction vessel. One of the

ports on the top of the vessel allowed for exit of gas to prevent pressure buildup. Gases were vented to the fume hood.

Surrogate spent acid solution was prepared by dissolving 50 grams of zinc chloride in 250 ml 12 N hydrochloric acid. All reagents used were certified ACS reagent grade obtained from Fisher Scientific. Once the feed had been added to the reaction vessel, the upper flange was put in place and instrumentation was added.

Mixing was started by agitation or air sparge directly to the vessel. Potassium hydroxide solution or magnesium hydroxide slurry, both used at a concentration of 6N, was added to the vessel using a Masterflex L/S Easy-Load II pump head, Masterflex speed controller and 1.41 mm Masterflex tubing.

The pH of the vessel contents was adjusted to 8.0 while the desired temperature was maintained. Temperature, time, and pH profiles were collected. Once the pH reached 8.0 the agitation was stopped and the contents of the vessel were drained through the valve at the bottom of the reactor and collected for filtration.

3.2 Effect of Agitation Type

Mechanical agitation was provided to the vessel by means of a marine propeller and the power input calculated using Equation 1.40. Air agitation

was provided to the vessel using compressed air with the power input calculated using Equation 1.39. The power for the two types of agitation was established at 0.0836 Watts.

To determine if there were any chemical effects from the air agitation, such as oxidation of the vessel contents, a comparison was performed using an inert gas. An experimental run was completed using compressed helium instead of compressed air at a neutralization temperature of 25°C using potassium hydroxide as the source of alkalinity. Two experimental runs were performed with the only difference between the two being the gas used for agitation.

3.3 Additive Effects

To investigate the influence of additives on the specific cake resistance, studies were done with different dosages of several additives. Zinc hydroxide slurry was prepared in the same manner as the slurry for the process parameter study, with the exception of a larger batch volume. Homogeneous samples of zinc hydroxide slurry (250 ml) were collected from the neutralization batch and put into a 600 ml beaker and mechanically agitated at 250 rpm with the temperature maintained at 25°C. A dose of precipitating agent was added and allowed to mix for 30 seconds. If required, a dose of coagulant M-25, was added and allowed to mix for 30 seconds along with one drop of flocculant

ANF-15 (diluted 1:100) added and the mixing increased to 600 rpm for 15 seconds. The mixing was then slowed to 20 rpm for 15 seconds, agitation was stopped, and the slurry collected for filtration. The wet solids were weighed and dried in a vacuum oven. After drying, the solids were weighed and saved for analysis using scanning electron microscopy.

3.4 Filtration

Once the zinc hydroxide slurry had been prepared by neutralization, two 250 ml homogeneous fractions of slurry were obtained and set aside. One of the 250 ml fractions of slurry was vacuum filtered 20 minutes after neutralization through the apparatus illustrated in Figure 6. The other homogeneous slurry fraction was filtered 24 hours after neutralization. Filtration was started immediately after all the slurry had been added to the device and vacuum was maintained at a constant 381 millimeters of Hg throughout the filtration step. All filtration steps were performed at 25°C. Filtrate volume and filtration time were recorded.

Using the time and volume data, physical property data, and the cross sectional area of the filtration apparatus, the specific cake resistance for the specific precipitate sample was calculated using Equation 1.36. The particles were weighed, dried and retained for mass balance calculations and qualitative analysis of the crystal habit using scanning electron microscopy. Mass

balances for each neutralization reaction are found in Appendix B. Scanning electron micrographs for selected experiments are found in Appendix C.

Figure 6. Filtration Apparatus

4. RESULTS

4.1 Observations

The precipitation reaction with the use of potassium hydroxide resulted in a gelatinous, high volume slurry. This slurry did not settle well and was hard to dewater. After filtration, the solids took a significant amount of time to dry and formed into large chunks. During the zinc precipitation reaction with potassium hydroxide, large solids were formed at a pH of 4-6. However, when the pH continued to rise, the solids became much smaller and the entire slurry appeared very dense and white.

The precipitation reaction with the use of magnesium hydroxide resulted in a slurry that settled considerably faster than the potassium hydroxide precipitates. In general, the solids filtered better and were easier to dry and the dry solids were free flowing as opposed to clumps. After nearly a stoichiometric amount of magnesium hydroxide had been added, the pH rose rapidly from below 1.0 to above 5.0 where solids began to form. When adjusted further, it took substantial time to reach a final value due to the buffering effect of the weak base.

An observation from the reaction with magnesium hydroxide was the change in temperature during the reaction. After the reaction had proceeded for 2.5 hours, the addition of magnesium hydroxide was discontinued. The

reaction vessel contents were at a pH of 6.08 and had an observed temperature of 23.2°C. After discontinuing the circulating bath and continuing to agitate for another 2.5 hours the pH increased to 7.82 and the temperature was observed at 24.2°C. This observation provides a qualitative idea of the length of time required for complete reaction with $\text{Mg}(\text{OH})_2$.

Because of the 5-hour neutralization time required for $\text{Mg}(\text{OH})_2$, its routine use might be a processing disadvantage. The time can be shortened, but it requires adding a large excess of reagent. This excess hydroxide will speed up neutralization but not result in higher pH levels. It will, however, result in large filter cakes and greater values for the specific cake resistance of the slurry due to the presence of undissolved $\text{Mg}(\text{OH})_2$.

4.2 Discussion of Results

The data for the filtration measurements can be found in Appendix A along with plots of filtrate volume accumulation over time which were used to calculate specific cake resistance, α (see Table 5 for the relevant Appendix figure). The specific cake resistance values for each experimental run are shown in Tables 6 and 7 and are listed in increasing order. These tables are a result of the statistical process parameter study where specific cake resistance was measured on a fraction of the zinc hydroxide slurry at a particle age of 20 minutes and a particle age of 24 hours. The specific cake resistance values are

generally equivalent except for minor differences for some of the values.

Table 5 . Relevant Appendix Figures for Process Parameter Study

Run	Neutralization Temperature	Alkalinity Source	Agitation Type	Appendix	Figure	
				Filtration Data	Mass Balance	SEM Micrograph
2	50	Mg(OH) ₂	Mechanical	A-3, 4	B-2	C-2
1	25	Mg(OH) ₂	Mechanical	A-1, 2	B-1	C-1
3	70	Mg(OH) ₂	Air	A-5, 6	B-3	C-3
5	70	KOH	Mechanical	A-9, 10	B-5	C-5
7	10	Mg(OH) ₂	Air	A-13, 14	B-7	C-7
6	25	KOH	Air	A-11, 12	B-6	C-6
8	10	KOH	Mechanical	A-15, 16	B-8	C-8
4	50	KOH	Air	A-7, 8	B-4	C-4

Table 6. Results of Process Parameters Study for Zinc Hydroxide Precipitates Filtered at a Particle Age of 20 Minutes

Run	Temperature (°C)	Alkalinity Source	Agitation Type	Specific Cake Resistance (m/kg) × 10 ⁻¹⁰
2	50	Mg(OH) ₂	Mechanical	0.50
1	25	Mg(OH) ₂	Mechanical	1.29
3	70	Mg(OH) ₂	Air	2.98
5	70	KOH	Mechanical	4.17
7	10	Mg(OH) ₂	Air	6.87
6	25	KOH	Air	52.49
8	10	KOH	Mechanical	53.66
4	50	KOH	Air	53.78

The results of the chemical additives study can be found in Table 9.

Data and calculations for the individual experiments are found in Appendix A (see Table 8 for the relevant Appendix figure) The specific cake resistance values for the process parameter study cannot be directly compared to the specific cake resistance values for the additive study because of differences in

Table 7. Results of Process Parameter Study for Zinc Hydroxide Precipitates Filtered at a Particle Age of 24 Hours

Run	Temperature (°C)	Alkalinity Source	Agitation Type	Specific Cake Resistance (m/kg) $\times 10^{-10}$
2	50	Mg(OH) ₂	Mechanical	0.32
1	25	Mg(OH) ₂	Mechanical	1.82
3	70	Mg(OH) ₂	Air	3.05
5	70	KOH	Mechanical	3.92
7	10	Mg(OH) ₂	Air	4.02
4	50	KOH	Air	46.82
6	25	KOH	Air	53.47
8	10	KOH	Mechanical	68.34

Table 8. Relevant Appendix Figures for Chemical Additives Study

Run	Alkalinity Source	Precipitatin g Agent	Dose (wt%)	Appendix	Figure	
				Filtration Data	Mass Balance	SEM Micrograph
K	KOH	None	-	A-19	B-10	C-9
KCP1	KOH	CP-PLUS	1%	A-20	B-10	C-10
KCP2	KOH	CP-PLUS	2%	A-21	B-10	
KCP4	KOH	CP-PLUS	4%	A-22	B-10	
KSP1	KOH	SP-PLUS	1%	A-23	B-10	C-11
KSP2	KOH	SP-PLUS	2%	A-24	B-10	
KSP4	KOH	SP-PLUS	4%	A-25	B-10	
KT1	KOH	THIO-RED	1%	A-26	B-10	
KT2	KOH	THIO-RED	2%	A-27	B-10	
KT4	KOH	THIO-RED	4%	A-28	B-10	C-12
M	Mg(OH) ₂	None	-	A-29	B-11	C-13
MCP2	Mg(OH) ₂	CP-PLUS	2%	A-30	B-11	
MCP4	Mg(OH) ₂	CP-PLUS	4%	A-31	B-11	
MCP8	Mg(OH) ₂	CP-PLUS	8%	A-32	B-11	C-14
MSP2	Mg(OH) ₂	SP-PLUS	2%	A-33	B-11	
MSP4	Mg(OH) ₂	SP-PLUS	4%	A-34	B-11	
MSP8	Mg(OH) ₂	SP-PLUS	8%	A-35	B-11	C-15
MT2	Mg(OH) ₂	THIO-RED	2%	A-36	B-11	
MT4	Mg(OH) ₂	THIO-RED	4%	A-37	B-11	
MT8	Mg(OH) ₂	THIO-RED	8%	A-38	B-11	C-16

slurry preparation. It appears from Table 9 that any additive used with precipitates from $\text{Mg}(\text{OH})_2$ produces cakes with specific cake resistances at least an order of magnitude smaller than those with no additive.

Table 9. Results of Additive Study

Run	Alkalinity Source	Precipitating Agent	Dose (wt %)	Specific Cake Resistance $(\text{m/kg}) \times 10^{-10}$
MT2	$\text{Mg}(\text{OH})_2$	THIO-RED	2%	2.49
MSP8	$\text{Mg}(\text{OH})_2$	SP-Plus	8%	2.69
MT4	$\text{Mg}(\text{OH})_2$	THIO-RED	4%	2.69
MSP4	$\text{Mg}(\text{OH})_2$	SP-Plus	4%	3.09
MCP8	$\text{Mg}(\text{OH})_2$	CP-Plus	8%	3.17
MT8	$\text{Mg}(\text{OH})_2$	THIO-RED	8%	3.49
MCP2	$\text{Mg}(\text{OH})_2$	CP-Plus	2%	3.49
MCP4	$\text{Mg}(\text{OH})_2$	CP-Plus	4%	3.63
MSP2	$\text{Mg}(\text{OH})_2$	SP-Plus	2%	3.82
M	$\text{Mg}(\text{OH})_2$	None	-	5.57
KCP1	KOH	CP-Plus	1%	47.81
KT2	KOH	THIO-RED	2%	51.36
KCP2	KOH	CP-Plus	2%	51.78
K	KOH	None	-	62.53
KSP1	KOH	SP-Plus	1%	80.90
KT1	KOH	THIO-RED	1%	82.81
KSP4	KOH	SP-Plus	4%	86.63
KCP4	KOH	CP-Plus	4%	142.55
KT4	KOH	THIO-RED	4%	2423.00
KSP2	KOH	SP-Plus	2%	3051.40

4.2.1 Statistical Analysis

An analysis of variance for the process parameter fractional factorial experiment was completed and is shown in Table 10. In order to allow for multiple evaluations of specific cake resistance, it was assumed that particle

age did not influence filterability. The time required for each filtration was relatively long, approximately 1 hour, and thus particles were continually aging. This assumption, made replication possible and is valid since the values of specific cake resistance illustrated in Tables 6 and 7 are generally in agreement.

An analysis of variance revealed that the neutralization temperature and the source of alkalinity were statistically significant at a 95% confidence level. The type of agitation was not a statistically significant factor influencing the specific cake resistance of zinc hydroxide precipitates and the filterability of the slurry was not significantly impacted by the gas used for agitation. The effect of additives was not a part of the statistical evaluation.

Table 10. ANOVA Table for Fractional Factorial Process Parameter Study

Source	Degrees Freedom	Sum of Squares	Mean Squares	F value	F critical
Temperature	3	2.03E+23	6.74E+22	4.14	3.71
Hydroxide	1	6.23E+23	6.23E+23	38.29	4.96
Agitation	1	4.99E+22	4.99E+22	3.07	4.96
Error	10	1.63E+23	1.63E+22		
Total	15	1.04E+24			

4.2.2 Temperature

The temperature of acid neutralization had a statistically significant impact on the specific cake resistance of zinc hydroxide precipitates. For most of the experiments, operation at elevated neutralization temperatures led to decreases in the specific cake resistance. These results are consistent with those found for similar studies (Vian, Rodriguez and Guardiola 1983). Higher temperatures resulted in decreased saturation which, in turn, led to increased growth rates and decreased nucleation rates. In addition, the slow cooling of the slurry may have resulted in increased growth by allowing controlled integration of molecules into the site.

4.2.3 Alkalinity Source

The source of alkalinity was also shown to have a statistically significant influence on the filterability of zinc hydroxide precipitates. The use of magnesium hydroxide resulted in zinc hydroxide precipitates with lower specific cake resistance values than those obtained by using potassium hydroxide. These results are consistent with other findings that have shown that precipitates obtained with the use of potassium hydroxide are gelatinous and difficult to filter (Dow Chemical Company 1996). Similar values for specific cake resistance were obtained for both magnesium hydroxide and potassium hydroxide when operating at a neutralization temperature of 70°C.

4.2.4 Agitation Type

The type of mixing in this study did not have a significant impact on the specific cake resistance. Although many studies have been done to examine the effects of various degrees of mixing on the resulting precipitate crystal habit, there is no evidence to suggest that studies have been done to compare air agitation with mechanical agitation. Studies to examine the degree of mixing have revealed that particles are significantly impacted by degree of mechanical mixing. Additionally, in this study the use of an inert gas for agitation compared to air agitation did not result in any statistical effect on specific cake resistance.

4.2.5 Particle Age

Although determination of the effect of particle age on the filterability of zinc hydroxide precipitates in this study was not possible, there is evidence in the literature suggesting that particle age can influence morphology. (Takiyama and Ishii 1981, Sato and Nakamura 1982). The authors have reported that morphological changes occur in the precipitates of cadmium hydroxides as they are aged. The morphology of the precipitates immediately after mixing the reagents was observed to be rectangular lamellar crystals. After the particles has aged in the mother liquor, the rectangular crystals began to dissolve and rearrange to form a fibrous structure. After several hours in the

mother liquor, stable hexagonal crystals were formed. In addition, Sato and Nakamura (1982) found that gallium hydroxide precipitates transform from amorphous particle to crystalline α -gallium hydroxide during aging.

Aging may also result in a smaller mean particle size. Agglomerates may disengage or small crystals adhering to the faces of large crystal may wash off (Sarig and Mullin 1980). There is also evidence suggesting the existence of an optimum particle age which yields maximum crystal size (Nyvlt and Zacek 1993). For short aging times, the crystal size increases with time. However, with longer times, an inverse dependence exists. The author attributes the decrease in particle size to secondary nucleation and breakage.

Although particle age may influence the filterability of zinc hydroxide precipitates, it was not possible in this study to investigate the influence. The filterability of zinc hydroxide precipitates was measured at a particle age of 20 minutes and 24 hours with generally similar values for each. Control of particle age in the future may help to determine the effect on specific cake resistance, although control of particle age in an industrial setting may not be feasible.

4.2.6 Chemical Additives

The use of chemical additives in conjunction with hydroxide precipitation resulted in lower specific cake resistance and improved

filterability of the zinc hydroxide slurries. The most significant improvements resulted when magnesium hydroxide was used as the alkalinity source during neutralization (see Table 9). In addition to precipitating agents, coagulants and flocculants also appeared to be effective in improving filterability. Dosages of these additives were based on manufacturers' recommendations and were not optimized. It is possible that a study of coagulant/flocculant dosage variation would lead to further improvements in filterability. Optimization of chemical additives is dependent not only upon dosage but also upon cost. The cost of the additives manufactured by ETUS, Inc. are listed in Table 11.

Table 11. Chemical Additive Costs

Chemical Additive	Price/55-gallon drum
SP-PLUS	\$595.00
CP-PLUS	\$870.00
THIO-RED	\$495.00
M-25	\$346.50
ANF-15	\$561.00

4.3 Equilibrium Concentration Diagrams

The equilibrium concentration diagrams (Figures 1 and 2) predict the formation of precipitates over a range of pH. The diagrams indicate formation of zinc hydroxide precipitates beginning at a pH of approximately 5. This prediction is consistent with experimental observations. During the

neutralization reaction, solids formation began at a pH of approximately 5 and continued until the neutralization was concluded at a pH of 8.0.

4.4 Crystal Habit and Scanning Electron Micrographs

It is quite uncommon for hydroxide precipitates to consist solely of discrete crystalline particles. Often the particles grow together during their formation in a variety of ways. Agglomerated particles occur frequently in hydroxide precipitation and may even account for the majority of particles. It is clear from the scanning electron micrographs of zinc hydroxide precipitates that the majority of particles are agglomerates. Scanning electron micrographs for all fractional factorial experimental runs and selected additive study experimental runs are found in Appendix C. A precise determination of the crystal habit of zinc hydroxide precipitates using the scanning electron micrographs was not possible, due in part, to the formation of agglomerates. Furthermore, the particles exist on a micron scale which makes determination of crystal habit difficult.

The images do provide important information about the nature and relative size of the agglomerates. The zinc hydroxide precipitates that had the lowest specific cake resistance values were the experiments neutralized with magnesium hydroxide and the experiment neutralized with potassium hydroxide at 70°C. It is clear from the micrographs (see Appendix Figures

C-1, C-2, C-3, C-5, C-7, C-13, C-14, C-15, C-16) that the precipitates for these experiments consist of free-flowing particles. Although they are agglomerates, these precipitates tended not to cake and form lumps when dried. The zinc hydroxide precipitates formed at moderate to low temperatures with the use of potassium hydroxide (see Appendix Figures C-4, C-6, C-8, C-9, C-10, C-11, C-12) tended to form dense cakes and were not free-flowing which limited their ability to be effectively filtered.

5. CONCLUSIONS

Several conclusions can be drawn as a result of this investigation of the effects of process parameters and chemical additives on the specific cake resistance of zinc hydroxide precipitates:

1. Hydroxide precipitation at elevated neutralization temperatures results in slurries with improved filterability.
2. Over the range of temperatures studied, the use of magnesium hydroxide as a neutralization agent is more effective than potassium hydroxide in producing hydroxide precipitates that have lower specific cake resistance values.
3. The type of agitation, air or mechanical, does not have a statistical effect on specific cake resistance values of zinc hydroxide precipitates.
4. The use of chemical additives in conjunction with hydroxide precipitation results in zinc hydroxide precipitates with greatly reduced specific cake resistance values compared to the precipitates with no additive.

APPENDIX A FILTRATION DATA AND SPECIFIC CAKE RESISTANCE

Figure A-1. Specific Cake Resistance for Experimental Run #1 Aged 20 Minutes

Specific Cake Resistance Calculation

Run	1b		
Area(m ²)	0.002374		
Mass Dry Solids(kg)	0.01838		
Pressure(N/m ²)	59652.75		
Volume of Filtrate(m ³)	0.00005	0.0001	0.00015
Time(s)	125	285	425
Viscosity(N s/m ²)	0.001002		
Volume (m ³)	0.00005	0.0001	0.00015
t/v	2500000	2850000	2833333

Slope	3.33E+09
intercept	2.53E+06
cake resistance(m/kg)	1.824E+10
medium resistance(1/m)	3.576E+11

Figure A-2. Specific Cake Resistance for Experimental Run #1 Aged 24 Hours

Specific Cake Resistance Calculation

Run	2		
Area(m ²)	0.002374		
Mass Dry Solids(kg)	0.02016		
Pressure(N/m ²)	59652.75		
Volume of Filtrate(m ³)	0.00005	0.0001	0.00015
Time(s)	105	215	330
Viscosity(N s/m ²)	0.001002		
Volume (m ³)	0.00005	0.0001	0.00015
t/v	2100000	2150000	2200000

Slope	1.00E+09
intercept	2.05E+06
cake resistance(m/kg)	4.99E+09
medium resistance(1	2.9E+11

Figure A-3. Specific Cake Resistance for Experimental Run #2 Aged 20 Minutes

Figure A-4. Specific Cake Resistance for Experimental Run #2 Aged 24 Hours

Figure A-5. Specific Cake Resistance for Experimental Run #3 Aged 20 Minutes

Figure A-6. Specific Cake Resistance for Experimental Run #3 Aged 24 Hours

Figure A-7. Specific Cake Resistance for Experimental Run #4 Aged 20 Minutes

Figure A-8. Specific Cake Resistance for Experimental Run #4 Aged 24 Hours

Figure A-9. Specific Cake Resistance for Experimental Run #5 Aged 20 Minutes

Figure A-10. Specific Cake Resistance for Experimental Run #5 Aged 24 Hours

Figure A-11. Specific Cake Resistance for Experimental Run #6 Aged 20 Minutes

Specific Cake Resistance Calculation

Run	6b		
Area(m ²)	0.002374		
Mass Dry Solids(kg)	0.01506		
Pressure(N/m ²)	59652.75		
Volume of Filtrate(m ³)	0.00005	0.0001	0.00015
Time(s)	300	1080	2100
Viscosity(N s/m ²)	0.001002		
Volume (m ³)	0.00005	0.0001	0.00015
t/v	6000000	1.1E+07	1.4E+07

Slope	8.00E+10
intercept	2.27E+06
cake resistance(m/kg)	5.347E+11
medium resistance(1	3.208E+11

Figure A-12. Specific Cake Resistance for Experimental Run #6 Aged 24 Hours

Figure A-13. Specific Cake Resistance for Experimental Run #7 Aged 20 Minutes

Figure A-14. Specific Cake Resistance for Experimental Run #7 Aged 24 Hours

Figure A-15. Specific Cake Resistance for Experimental Run #8 Aged 20 Minutes

Specific Cake Resistance Calculation

Run	8b		
Area(m ²)	0.002374		
Mass Dry Solids(kg)	0.01797		
Pressure(N/m ²)	59652.75		
Volume of Filtrate(m ³)	0.00005	0.0001	0.00015
Time(s)	630	1980	3720
Viscosity(N s/m ²)	0.001002		
Volume (m ³)	0.00005	0.0001	0.00015
t/v	12600000	2E+07	2.5E+07

Slope	1.22E+11
intercept	6.87E+06
cake resistance(m/kg	6.834E+11
medium resistance(1	9.71E+11

Figure A-16. Specific Cake Resistance for Experimental Run #8 Aged 24 Hours

Figure A-17. Specific Cake Resistance for Experimental Run #9 Aged 20 Minutes

Figure A-18. Specific Cake Resistance for Experimental Run #9 Aged 24 Hours

Figure A-19. Specific Cake Resistance for Experimental Run K

Specific Cake Resistance Calculation

Run	KCP1		
Area(m ²)	0.002374		
Mass Dry Solids(kg)	0.016		
Pressure(N/m ²)	59652.75		
Volume of Filtrate(m ³)	0.00005	0.0001	0.00015
Time(s)	360	1110	2220
Viscosity(N s/m ²)	0.001002		
Volume (m ³)	0.00005	0.0001	0.00015
t/v	7200000	1.1E+07	1.5E+07

Slope	7.60E+10
intercept	3.43E+06
cake resistance(m/kg	4.781E+11
medium resistance(1	4.848E+11

Figure A-20. Specific Cake Resistance for Experimental Run KCP1

Figure A-21. Specific Cake Resistance for Experimental Run KCP2

Specific Cake Resistance Calculation

Run	KCP4		
Area(m ²)	0.002374		
Mass Dry Solids(kg)	0.01271		
Pressure(N/m ²)	59652.75		
Volume of Filtrate(m ³)	0.00005	0.0001	0.00015
Time(s)	440	1518	2940
Viscosity(N s/m ²)	0.001002		
Volume (m ³)	0.00005	0.0001	0.00015
t/v	8800000	1.5E+07	2E+07

Slope	1.80E+11
intercept	3.73E+06
cake resistance(m/kg	1.426E+12
medium resistance(1	5.272E+11

Figure A-22. Specific Cake Resistance for Experimental Run KCP4

Figure A-23. Specific Cake Resistance for Experimental Run KSP1

Specific Cake Resistance Calculation

Run	KSP2		
Area(m ²)	0.01484		
Mass Dry Solids(kg)	0.01289		
Pressure(N/m ²)	59652.75		
Volume of Filtrate(m ³)	0.00005	0.0001	0.00015
Time(s)	480	1590	2940
Viscosity(N s/m ²)	0.001002		
Volume (m ³)	0.00005	0.0001	0.00015
t/v	9600000	1.6E+07	2E+07

Slope	1.00E+11
intercept	5.03E+06
cake resistance(m/kg	3.051E+13
medium resistance(1	4.444E+12

Figure A-24. Specific Cake Resistance for Experimental Run KSP2

Figure A-25. Specific Cake Resistance for Experimental Run KSP4

Specific Cake Resistance Calculation

Run	KT1		
Area(m ²)	0.002374		
Mass Dry Solids(kg)	0.0141		
Pressure(N/m ²)	59652.75		
Volume of Filtrate(m ³)	0.00005	0.0001	0.00015
Time(s)	375	1380	2865
Viscosity(N s/m ²)	0.001002		
Volume (m ³)	0.00005	0.0001	0.00015
t/v	7500000	1.4E+07	1.9E+07

Slope	1.16E+11
intercept	1.87E+06
cake resistance(m/kg)	8.281E+11
medium resistance(1	2.643E+11

Figure A-26. Specific Cake Resistance for Experimental Run KT1

Figure A-27. Specific Cake Resistance for Experimental Run KT2

Specific Cake Resistance Calculation

Run	KT4		
Area(m ²)	0.01486		
Mass Dry Solids(kg)	0.01289		
Pressure(N/m ²)	59652.75		
Volume of Filtrate(m ³)	0.00005	0.0001	0.00015
Time(s)	270	960	1998
Viscosity(N s/m ²)	0.001002		
Volume (m ³)	0.00005	0.0001	0.00015
t/v	5400000	9600000	1.3E+07

Slope	7.92E+10
intercept	1.52E+06
cake resistance(m/kg)	2.423E+13
medium resistance(1	1.345E+12

Figure A-28. Specific Cake Resistance for Experimental Run KT4

Figure A-29. Specific Cake Resistance for Experimental Run M

Specific Cake Resistance Calculation

Run	MCP2		
Area(m ²)	0.002374		
Mass Dry Solids(kg)	0.02017		
Pressure(N/m ²)	59652.75		
Volume of Filtrate(m ³)	0.00005	0.0001	0.00015
Time(s)	150	340	555
Viscosity(N s/m ²)	0.001002		
Volume (m ³)	0.00005	0.0001	0.00015
t/v	3000000	3400000	3700000

Slope	7.00E+09
intercept	2.67E+06
cake resistance(m/kg)	3.493E+10
medium resistance(1	3.774E+11

Figure A-30. Specific Cake Resistance for Experimental Run MCP2

Figure A-31. Specific Cake Resistance for Experimental Run MCP4

Specific Cake Resistance Calculation

Run	MCP8		
Area(m ²)	0.002374		
Mass Dry Solids(kg)	0.01906		
Pressure(N/m ²)	59652.75		
Volume of Filtrate(m ³)	0.00005	0.0001	0.00015
Time(s)	135	320	495
Viscosity(N s/m ²)	0.001002		
Volume (m ³)	0.00005	0.0001	0.00015
t/v	2700000	3200000	3300000

Slope	6.00E+09
intercept	2.47E+06
cake resistance(m/kg)	3.169E+10
medium resistance(1	3.491E+11

Figure A-32. Specific Cake Resistance for Experimental Run MCP8

Figure A-33. Specific Cake Resistance for Experimental Run MSP2

Specific Cake Resistance Calculation

Run	MSP4		
Area(m ²)	0.002374		
Mass Dry Solids(kg)	0.01956		
Pressure(N/m ²)	59652.75		
Volume of Filtrate(m ³)	0.00005	0.0001	0.00015
Time(s)	120	280	450
Viscosity(N s/m ²)	0.001002		
Volume (m ³)	0.00005	0.0001	0.00015
t/v	2400000	2800000	3000000

Slope	6.00E+09
intercept	2.13E+06
cake resistance(m/kg)	3.088E+10
medium resistance(1	3.01E+11

Figure A-34. Specific Cake Resistance for Experimental Run MSP4

Figure A-35. Specific Cake Resistance for Experimental Run MSP8

Specific Cake Resistance Calculation

Run	MT2		
Area(m ²)	0.002374		
Mass Dry Solids(kg)	0.02024		
Pressure(N/m ²)	59652.75		
Volume of Filtrate(m ³)	0.00005	0.0001	0.00015
Time(s)	70	180	285
Viscosity(N s/m ²)	0.001002		
Volume (m ³)	0.00005	0.0001	0.00015
t/v	1400000	1800000	1900000

Slope	5.00E+09
intercept	1.20E+06
cake resistance(m/kg	2.487E+10
medium resistance(1	1.696E+11

Figure A-36. Specific Cake Resistance for Experimental Run MT2

Figure A-37. Specific Cake Resistance for Experimental Run MT4

Specific Cake Resistance Calculation

Run	MT8		
Area(m ²)	0.002374		
Mass Dry Solids(kg)	0.01899		
Pressure(N/m ²)	59652.75		
Volume of Filtrate(m ³)	0.00005	0.0001	0.00015
Time(s)	42	130	225
Viscosity(N s/m ²)	0.001002		
Volume (m ³)	0.00005	0.0001	0.00015
t/v	840000	1300000	1500000

Slope	6.60E+09
intercept	5.53E+05
cake resistance(m/kg	3.498E+10
medium resistance(1	7.816E+10

Figure A-38. Specific Cake Resistance for Experimental Run MT8

APPENDIX B MASS BALANCES

Run #1				
MASS BALANCE: SYSTEMS WITH Mg(OH) ₂				
2 HCl + 1 Mg(OH) ₂ -> 1 MgCl ₂ + 2 H ₂ O				
1 ZnCl ₂ + 1 Mg(OH) ₂ -> 1 MgCl ₂ + 1 Zn(OH) ₂				
IN:	moles	grams		
HCl		3 109.38		
H ₂ O	51.81101	932.5981		
ZnCl ₂	0.366892	50		
Mg(OH) ₂	4.462667	260.1735		
TOTAL		1352.152		
OUT:	moles	grams	%	
MgCl ₂	1.866892	177.7281	13.14439	
Zn(OH) ₂	0.366892	36.4617	2.696628	
H ₂ O	54.81101	986.5981	72.96667	
Mg(OH) ₂	2.595776	151.3337	11.19232	
TOTAL:		1352.122	100	
Slurry Weight:		1351.54		

Figure B-1. Mass Balance for Experimental Run 1#

Run #2				
MASS BALANCE: SYSTEMS WITH Mg(OH) ₂				
2 HCl + 1 Mg(OH) ₂ - 1 MgCl ₂ + 2 H ₂ O				
1 ZnCl ₂ + 1 Mg(OH) ₂ -> 1 MgCl ₂ + 1 Zn(OH) ₂				
IN:	moles	grams		
HCl		3	109.38	
H ₂ O	52.94582	953.0248		
ZnCl ₂	0.366892	50		
Mg(OH) ₂	4.605777	268.5168		
TOTAL		1380.922		
OUT:	moles	grams	%	
MgCl ₂	1.866892	177.7281	12.87053	
Zn(OH) ₂	0.366892	36.4617	2.640446	
H ₂ O	55.94582	1007.025	72.9257	
Mg(OH) ₂	2.738885	159.677	11.56333	
TOTAL:		1380.892	100	
Slurry Weight:		1380.55		

Figure B-2. Mass Balance for Experimental Run #2

Run #3				
MASS BALANCE: SYSTEMS WITH Mg(OH) ₂				
2 HCl + 1 Mg(OH) ₂ -> 1 MgCl ₂ + 2 H ₂ O				
1 ZnCl ₂ + 1 Mg(OH) ₂ -> 1 MgCl ₂ + 1 Zn(OH) ₂				
IN:	moles	grams		
HCl	3	109.38		
H ₂ O	47.39402	853.0923		
ZnCl ₂	0.366892	50		
Mg(OH) ₂	3.905151	227.6703		
TOTAL		1240.143		
OUT:	moles	grams	%	
MgCl ₂	1.866892	177.7281	14.33161	
Zn(OH) ₂	0.366892	36.4617	2.940192	
H ₂ O	50.39402	907.0923	73.14596	
Mg(OH) ₂	2.038259	118.8305	9.582236	
TOTAL:		1240.113	100	
Slurry Weight:		1249.08		

Figure B-3. Mass Balance for Experimental Run #3

Run #4				
MASS BALANCE: SYSTEMS WITH KOH:				
1 HCl + 1 KOH -> 1 KCl + 1 H ₂ O				
1 ZnCl ₂ + 2 KOH-> 2 KCl + 1 Zn(OH) ₂				
IN:	moles	grams		
HCl	3	109.38		
H ₂ O	52.57958	946.4325		
ZnCl ₂	0.366892	50		
KOH	4.422445	248.0992		
TOTAL		1353.912		
OUT:	moles	grams	%	
KCl	3.733783	278.3536	20.55967	
Zn(OH) ₂	0.366892	36.4617	2.693123	
H ₂ O	55.57958	1000.432	73.89364	
KOH	0.688662	38.63391	2.853566	
TOTAL:		1353.882	100	
Slurry Wt:	1288.06	1353		

Figure B-4. Mass Balance for Experimental Run #4

Run #5					
MASS BALANCE: SYSTEMS WITH KOH:					
		1 HCl +	1 KOH ->	1 KCl +	1 H ₂ O
		1 ZnCl ₂ +	2 KOH ->	2 KCl +	1 Zn(OH) ₂
IN:	moles	grams			
HCl		3	109.38		
H ₂ O	49.86699	897.6059			
ZnCl ₂	0.366892	50			
KOH	4.090655	229.4857			
TOTAL		1286.472			
OUT:	moles	grams	%		
KCl	3.733783	278.3536	21.63748		
Zn(OH) ₂	0.366892	36.4617	2.834306		
H ₂ O	52.86699	951.6059	73.97195		
KOH	0.356871	20.02047	1.556267		
TOTAL:		1286.442	100		
Slurry Weight:		1282.58			

Figure B-5. Mass Balance for Experimental Run #5

Run #6					
MASS BALANCE: SYSTEMS WITH KOH:					
		1 HCl +	1 KOH ->	1 KCl +	1 H ₂ O
		1 ZnCl ₂ +	2 KOH ->	2 KCl +	1 Zn(OH) ₂
IN:	moles	grams			
HCl		3	109.38		
H ₂ O	47.62461	857.2429			
ZnCl ₂	0.366892	50			
KOH	3.816376	214.0987			
TOTAL		1230.722			
OUT:	moles	grams	%		
KCl	3.733783	278.3536	22.61765		
Zn(OH) ₂	0.366892	36.4617	2.9627		
H ₂ O	50.62461	911.2429	74.04315		
KOH	0.082593	4.633472	0.376493		
TOTAL:		1230.692	100		
Slurry Wt:	1185.12	1230.12			

Figure B-6. Mass Balance for Experimental Run #6

Run #7				
MASS BALANCE: SYSTEMS WITH $\text{Mg}(\text{OH})_2$				
$2 \text{ HCl} + 1 \text{ Mg}(\text{OH})_2 - 1 \text{ MgCl}_2 + 2 \text{ H}_2\text{O}$				
$1 \text{ ZnCl}_2 + 1 \text{ Mg}(\text{OH})_2 \rightarrow 1 \text{ MgCl}_2 + 1 \text{ Zn}(\text{OH})_2$				
IN:	moles	grams		
HCl	3	109.38		
H ₂ O	48.53081	873.5545		
ZnCl ₂	0.366892	50		
Mg(OH) ₂	4.049007	236.0571		
TOTAL		1268.992		
OUT:	moles	grams	%	
MgCl ₂	1.866892	177.7281	14.00579	
Zn(OH) ₂	0.366892	36.4617	2.873349	
H ₂ O	51.53081	927.5545	73.09555	
Mg(OH) ₂	2.182115	127.2173	10.02531	
TOTAL:		1268.962	100	
Slurry Weight:		1266.8		

Figure B-7. Mass Balance for Experimental Run #7

Run #8				
MASS BALANCE: SYSTEMS WITH KOH:				
$1 \text{ HCl} + 1 \text{ KOH} \rightarrow 1 \text{ KCl} + 1 \text{ H}_2\text{O}$				
$1 \text{ ZnCl}_2 + 2 \text{ KOH} \rightarrow 2 \text{ KCl} + 1 \text{ Zn}(\text{OH})_2$				
IN:	moles	grams		
HCl	3	109.38		
H ₂ O	50.28812	905.1862		
ZnCl ₂	0.366892	50		
KOH	4.142165	232.3754		
TOTAL		1296.942		
OUT:	moles	grams	%	
KCl	3.733783	278.3536	21.4628	
Zn(OH) ₂	0.366892	36.4617	2.811425	
H ₂ O	53.28812	959.1862	73.95926	
KOH	0.408381	22.91019	1.766519	
TOTAL:		1296.912	100	
Slurry Wt:	1182.58	1296		

Figure B-8. Mass Balance for Experimental Run #8

Run #9				
MASS BALANCE: SYSTEMS WITH KOH:				
		1 HCl +	1 KOH ->	1 KCl + 1 H ₂ O
		1 ZnCl ₂ +	2 KOH->	2 KCl + 1 Zn(OH) ₂
IN:	moles	grams		
HCl		3	109.38	
H ₂ O	47.07919	847.4255		
ZnCl ₂	0.366892	50		
KOH	3.749664	210.3562		
TOTAL		1217.162		
OUT:	moles	grams	%	
KCl	3.733783	278.3536	22.86963	
Zn(OH) ₂	0.366892	36.4617	2.995707	
H ₂ O	50.07919	901.4255	74.06146	
KOH	0.015881	0.890912	0.073198	
TOTAL:		1217.132	100	
Slurry Wt:	1181.45	1217		

Figure B-9. Mass Balance for Experimental Run #9

Preparation of slurry for additives study				
MASS BALANCE: SYSTEMS WITH KOH:				
		1 HCl +	1 KOH ->	1 KCl + 1 H ₂ O
		1 ZnCl ₂ +	2 KOH->	2 KCl + 1 Zn(OH) ₂
IN:	moles	grams		
HCl		3	109.38	
H ₂ O	83.64843	1505.672		
ZnCl ₂	0.366892	50		
KOH	8.222635	461.2898		
TOTAL		2126.342		
OUT:	moles	grams	%	
KCl	3.733783	278.3536	13.09091	
Zn(OH) ₂	0.366892	36.4617	1.714786	
H ₂ O	86.64843	1559.672	73.35104	
KOH	4.488852	251.8246	11.84326	
TOTAL:		2126.312	100	
Slurry Wt:	2479.15	2129.15		

Figure B-10. Mass Balance for Additive Experiments Using KOH

Preparation of slurry for additives study				
MASS BALANCE: SYSTEMS WITH Mg(OH) ₂				
2 HCl + 1 Mg(OH) ₂ - 1 MgCl ₂ + 2 H ₂ O				
1 ZnCl ₂ + 1 Mg(OH) ₂ - 1 MgCl ₂ + 1 Zn(OH) ₂				
IN:	moles	grams		
HCl	3	109.38		
H ₂ O	88.11212	1586.018		
ZnCl ₂	0.366892	50		
Mg(OH) ₂	9.045513	527.3534		
TOTAL		2272.752		
OUT:	moles	grams		
MgCl ₂	1.866892	177.7281	7.820055	
Zn(OH) ₂	0.366892	36.4617	1.604319	
H ₂ O	91.11212	1640.018	72.16098	
Mg(OH) ₂	7.178621	418.5136	18.41464	
TOTAL:		2272.722	100	
Slurry Wei	2626.5	2276.5		

Figure B-11. Mass Balance for Additive Experiments Using Mg(OH)₂

APPENDIX C SCANNING ELECTRON MICROGRAPHS

Figure C-1. Scanning Electron Micrograph Magnification 100-Run 1

Figure C-2. Scanning Electron Micrograph Magnification 100-Run 2

Figure C-3. Scanning Electron Micrograph Magnification 100-Run 3

Figure C-4. Scanning Electron Micrograph Magnification 100-Run 4

Figure C-5. Scanning Electron Micrograph Magnification 100-Run 5

Figure C-6. Scanning Electron Micrograph Magnification 100-Run 6

Figure C-7. Scanning Electron Micrograph Magnification 100-Run 7

Figure C-8. Scanning Electron Micrograph Magnification 100-Run 8

Figure C-9. Scanning Electron Micrograph Magnification 100-Run K

Figure C-10. Scanning Electron Micrograph Magnification 100-Run KCP1

Figure C-11. Scanning Electron Micrograph Magnification 100-Run KSP1

Figure C-12. Scanning Electron Micrograph Magnification 100-Run KT4

Figure C-13. Scanning Electron Micrograph Magnification 100-Run M

Figure C-14. Scanning Electron Micrograph Magnification 100-Run MCP8

Figure C-15. Scanning Electron Micrograph Magnification 100-Run MSP8

Figure C-16. Scanning Electron Micrograph Magnification 100-Run MT8

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