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Determination of Reaction Kinetics of Barium Sulfide with Sodium
Carbonate and Sodium Sulfate to Reduce Deadload in the Recovery Cycle

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Abstract

The following study deals with the characteristics of the reaction to form BaSO_4 and BaCO_3 from Na_2SO_4 and Na_2CO_3 , respectively, using BaS as the other reactant. These reactions would theoretically increase the efficiency of the chemical recovery process in papermaking to near 100% by completely converting Na_2SO_4 to Na_2S and Na_2CO_3 to NaOH .

Kinetic data were collected, and it was determined that both reactions were overall first order with rate constants of 0.037s^{-1} for the formation of BaSO_4 and 0.021s^{-1} for the formation of BaCO_3 . Also, it was found that both reactions go to completion in under three minutes. The heats of reaction were studied and found to be negligible.

BaSO_4 particle sizes averaged approximately $4.5\mu\text{m}$ and remained steady with respect to time while BaCO_3 particle sizes were approximately $21\mu\text{m}$ initially, but decreased over the course of several days. BaCO_3 formed agglomerates which began to break down immediately, but BaSO_4 did not form agglomerates at all. No explanation for why BaCO_3 formed agglomerates and BaSO_4 did not could be determined experimentally or found in the literature. Attempts to increase the particle size of BaSO_4 included seeding the initial solution with BaSO_4 crystals and increasing the concentration of reactants from 0.100M solutions each to 0.292M for BaS and 1.31M for the sodium salts. Both seeding and increased reactant concentration had no effect on particle size.

The settling rates of BaSO_4 and BaCO_3 particles were also studied. BaSO_4 exhibited mainly discrete and some flocculant settling characteristics, and the suspension as a whole settled quickly with some smaller particles remaining in suspension for a lengthy period of time. Hindered and mainly compression settling occurred with BaCO_3 because of the agglomerates that formed due to strong particle-particle interactions. BaCO_3 settled slowly, but virtually no particles remained in suspension after the bulk of the particles settled.

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Introduction

At present, the Kraft process is the most widely used papermaking process in the United States. It employs white liquor, a mixture of sodium hydroxide (NaOH) and sodium sulfide (Na_2S), to pulp the wood chips. Black liquor, the term given to the resulting chemicals after the pulp has been washed, contains significant amounts of sodium carbonate (Na_2CO_3) and sodium sulfate (Na_2SO_4). After the black liquor is burned in the recovery boiler, smelt is collected at the bottom of the recovery boiler and dissolved in water to form green liquor. Green liquor contains Na_2CO_3 which is causticized to regenerate NaOH , while the Na_2SO_4 is reduced in the recovery boiler smelt bed to regenerate Na_2S [5, 15].

The resulting white liquor is recycled to be used in pulping more wood chips. Causticization is a reversible process with typical conversions of the Na_2CO_3 to desirable NaOH of 80-85% [5]. The rest exits with the white liquor to be used to pulp more wood chips. Na_2CO_3 and Na_2SO_4 are deadload chemicals that contribute nothing to the process while consuming large amounts of energy and occupying space which decreases the capacity and efficiency of the entire process. However, the remaining quantities of Na_2CO_3 and Na_2SO_4 are very difficult to remove from white liquor because of their high solubilities [7].

A solution to this problem is to drive the causticization reaction to completion which can be accomplished by removing one or more products from solution. This phenomenon is known as LaChatelier's Principle [11]. Barium sulfide (BaS) is proposed as a replacement for calcium hydroxide because when it is reacted with Na_2CO_3 and

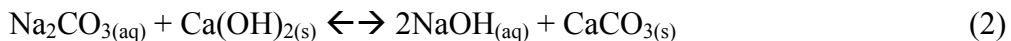
Na_2SO_4 , the products of the reactions – barium carbonate (BaCO_3) and barium sulfate (BaSO_4) – are insoluble [12]. Because BaCO_3 and BaSO_4 are insoluble, they precipitate out of solution which removes them from the equilibrium expression. By LaChatelier's Principle, the equilibrium continually proceeds to the product side and, as a result, the reactions go to completion and all of the deadload chemicals are consumed [11].

Equimolar solutions of BaS and Na_2CO_3 (or Na_2SO_4) were reacted to determine the extent of the reaction. To be completely feasible, the BaCO_3 and BaSO_4 products also must be able to be removed easily from the process. Therefore, the particle sizes and settling rates of the products were determined, and the heat effects of these reactions were also determined.

Literature Review

Causticizing in Black Liquor Recovery

The purpose of the chemical recovery process is to regenerate NaOH and Na₂S to be used in white liquor. After the wood chips are cooked in white liquor in the digester, the soluble products of pulping are washed from the pulp. The resulting black liquor is run through a series of multiple effect evaporators to increase the solids content of the liquor. This concentrated black liquor is sprayed in the recovery boiler where it is burned to produce energy. Also, this is where the Na₂SO₄ is reduced to Na₂S [5]. The molten solids collected at the bottom of the recovery boiler are called smelt, and it is dissolved in water which forms green liquor. Some insoluble material, known as dregs, remains in the green liquor. After the dregs are removed from the green liquor in the green liquor clarifier, the liquor is sent to the slaker where the Na₂CO₃ is reacted with calcium hydroxide (Ca(OH)₂) to regenerate NaOH [15]. The entire causticizing process is illustrated in equations (1), (2), and (3) [5].



Calcium oxide (CaO), or lime, reacts with water to form Ca(OH)₂. Next, the Ca(OH)₂ is reacted with the Na₂CO₃ in the causticizers to regenerate NaOH. Calcium carbonate (CaCO₃), or lime mud, is decomposed in a lime kiln to regenerate the CaO in a process known as calcining. Calcining is a slow, endothermic process, and the reversible causticizing reaction (2) is only about 80-85% efficient [5].

Le Chatelier's Principle

Le Chatelier's Principle states that when a system initially at equilibrium is disturbed, it tends to adjust itself to achieve the initial equilibrium [11]. For example, consider a reversible reaction at equilibrium. Removing a product from the reaction mixture will upset the equilibrium and cause the forward reaction to proceed to make up for the product that was removed. Similarly, removing a reactant from the reaction mixture will cause the reverse reaction to proceed to make up for the reactant that was removed. Now, consider the main reactions of this experiment illustrated in equations (4) and (5).



If all of the species were soluble in water, then the reactions would achieve equilibrium, and there would be amounts of all species in the final solution. However, since BaCO_3 and BaSO_4 are insoluble, they precipitate out of solution which effectively eliminates them from the equilibrium expression. As a result, the equilibria of both reactions are never achieved, so both reactions are theoretically driven to completion [11].

Reaction Conversion Determination

As is illustrated in equation (4), the soluble reactants, BaS and Na_2CO_3 , ionize in solution but when mixed together, an insoluble precipitate, BaCO_3 , forms. Since the coefficients of all species in the reaction are one, if equimolar solutions of BaS and Na_2CO_3 are reacted, then the same number of moles of BaCO_3 should be formed. This

theoretical amount is determined and compared to the actual amount of BaCO_3 formed. The percentage of actual BaCO_3 formed over theoretical BaCO_3 serves as the extent of reaction. This methodology is used as the extent of reaction for BaSO_4 as well.

Determination of Reaction Kinetics

Increased ion concentrations in solution increase the conductivity of a solution. As a reaction proceeds in which a solid precipitate is formed, the ions are consumed so the conductivity of the solution should theoretically decrease in proportion to the decrease in ion concentration. However, the measured conductivity may also be influenced by the solid precipitate particles dispersed in the solution. This additional effect will be more severe as the reaction nears completion because more precipitate is formed, so the measured rate of reaction will be different from the actual rate of reaction [11].

The integral method of analysis is normally used to find the kinetic rate constant, k , when the reaction order is known, but it may also be used when the reaction order is unknown [4]. This method involves comparing experimental concentration versus time data to theoretical concentration versus time data. Equation (6) is the kinetic rate law for first order reactions

$$-r_A = -dC_A/dt = kC_A \quad (6)$$

where $-r_A$ is the rate law, $-dC_A/dt$ is the rate of disappearance of reactant A, k is the rate constant, and C_A is the concentration of reactant A. Note that other reactants may be present, but the concentrations of those reactants are irrelevant since they are not

present in the rate law expression. It is said that the reaction is zero order with respect to those reactants. Equation (6) is integrated to the form in equation (7)

$$\ln \frac{C_{A0}}{C_A} = kt \quad (7)$$

where C_{A0} is the initial concentration of A. Experimental data are used to find $\ln(C_{A0}/C_A)$, and it is plotted versus time. If the reaction is actually first order, then the resulting plot will be a straight line with y-intercept near zero (allowing for experimental error) and slope k . If, however, the plot is not a straight line, then the reaction is not first order [4].

Similarly, a second order reaction has a kinetic rate law in the form of equation (8) if equimolar concentrations of reactants A and B are used ($C_A = C_B$) [6].

$$-r_A = -dC_A/dt = kC_AC_B = kC_A^2 \quad (8)$$

This expression is integrated to the form in equation (9).

$$\frac{1}{C_A} - \frac{1}{C_{A0}} = kt \quad (9)$$

$1/C_A$ is plotted against time, and, if the reaction is second order, the resulting plot should have slope k and y-intercept $1/C_{A0}$. The integral method of analysis tends to smooth inaccuracies due to experimental error [4].

To determine the reaction order with respect to individual reactants, the method of excess is used. The method of excess involves using a very high concentration of one reactant relative to the other. As the reaction proceeds, the concentration of the limiting reagent changes noticeably while the concentration of the reagent in excess changes very little. Thus, the concentration of the reagent in excess can be considered constant over the course of the reaction, and its value is lumped into the rate constant. This procedure

is then repeated exactly except that the reactant that was in excess now becomes the limiting reagent. From the results of this test, the reaction order with respect to each reactant is known, and the kinetic rate constant can be calculated by determining the reaction rate at known reactant concentrations [4].

Solid Precipitation and Particle Growth

Precipitation occurs when the concentration of a solid in solution is above the solubility limit of that compound in said solution. The process of precipitation can be divided into four steps: nucleation, crystal growth, aggregation or agglomeration, and breakup [8]. These steps can occur simultaneously in all systems, but some may be more dominant relative to others depending on the specific system under study [3].

Nucleation is defined as the generation of thermodynamically stable nuclei [13] and can be divided into two main categories: homogeneous nucleation and heterogeneous nucleation. Homogeneous nucleation occurs when no solid interface is present and can happen when a new particle is formed from two ions or when the concentration in solution rises above the solubility limit. Heterogeneous nucleation occurs in the presence of a solid surface that has a lower surface energy than that of a new solute particle. These two main forms of nucleation are unlikely to happen simultaneously, and most nucleation is heterogeneous [3].

The growth of solid particles during precipitation depends on a number of factors including, but not limited to, physical surface characteristics, concentration, intermolecular forces, and degree of agitation [3, 2, 8]. If the surface of a crystal is rough, the growth rate of that crystal will be larger than that of a crystal with a relatively

smooth surface. A particle added to a rough surface has a greater chance of adsorbing to a site with a higher binding energy than a smooth surface. Consider the simple illustration in Figure 1 below. On the smooth surface, the particle can bind on only one side as indicated by A while on the rough surface, the particle can bind on two or three sides as indicated by B and C, respectively, on this simple two-dimensional illustration [3].

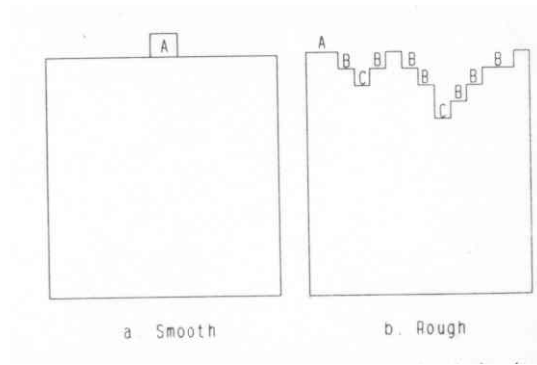


Figure 1: Interface between a solid surface and a particle suspended in solution [3].

Ion concentration also affects crystal growth. It has been found that there exists a critical ion concentration at which the mean particle size is a maximum for BaSO_4 formed from Na_2SO_4 and BaCl_2 [18]. Below the critical point, an insufficient quantity of ions is present in solution to chemisorb onto existing crystal surfaces before a new crystal is formed. Above the critical point, the unreacted ions interfere with adsorption of particles which slows crystal growth by reducing the electrical double layer which is discussed later. Along these same lines, a critical stirrer speed also exists below which not enough agitation is provided to adequately mix the suspension and above which exists too much shear force for the particles to adsorb onto a surface [2]. It is logical to conclude that a similar behavior exists for the present study although the exact critical concentrations and degree of agitation are unique to specific systems.

Particles in suspension are influenced to a large degree by attractive and repulsive forces. Attractive forces are mainly van der Waals interactions while the repulsive forces are caused by interactions of the electric double layers surrounding the individual particles [8]. When a particle is introduced into a system, it usually takes on a local surface charge, and it attracts particles of opposite charge in the solution, known as counterions, to balance the charge. The counterions are bound tightly to the surface of the particle due to strong van der Waals and electrostatic forces, and this layer of counterions is called the Stern Layer which is illustrated in Figure 2.

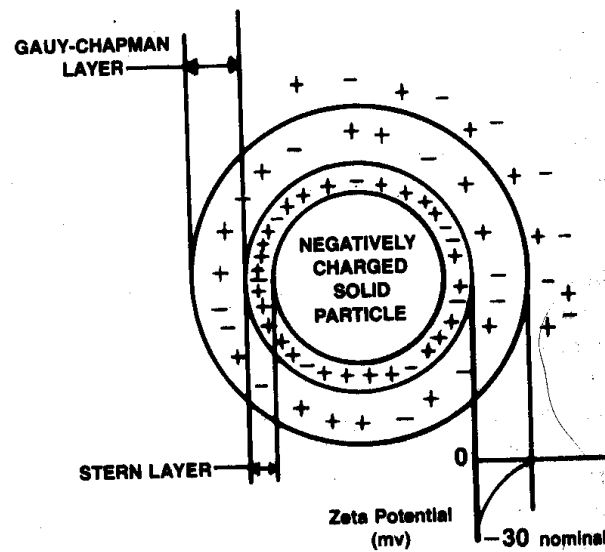


Figure 2: Illustration of zeta potential of a negatively charged particle in suspension [15].

The concentration of counterions in the Stern Layer in turn causes another layer of charged particles to form around it. This outer layer is called the Gauy-Chapman Layer, but it is wider and more diffuse than the Stern Layer. The combination of these two layers is called the electric double layer, and surrounding the Gauy-Chapman Layer is the bulk solution [14].

Zeta potential, as shown in Figure 2, is defined as the potential at the interface between the Stern Layer and the Gouy-Chapman Layer [14]. Strong van der Waals forces between particles lead to a faster rate of crystal growth while strong double layer interactions lead to slower crystal growth because of the repulsion [8]. However, it should be noted that while these factors are important, it has already been discussed that other factors such as concentration and agitation influence crystal growth, and certain factors may be more important than others for different systems.

Finally, the phenomenon of agglomeration also influences particle size. Agglomeration is caused by the collision of particles in a suspension, those particles adhering to each other due to weak van der Waals forces, and then solidifying the agglomerate by crystal growth that chemically bonds the particles together. All three of these steps occur but the agglomerate is subject to disagglomeration if shear forces break up the agglomerate before the bonds are strong enough to hold it together. The degree of agglomeration is influenced in much the same way as normal particle growth in that agitation is needed to force particles to collide, but it cannot be too high otherwise disagglomeration will occur [10].

All particle growth mechanisms are affected by similar sample properties such as concentration, intermolecular forces, shear, and physical characteristics of the particle surface. However, since different chemical species vary with respect to these properties, some species may exhibit certain particle growth mechanisms while showing little or no evidence of others. For example, strong agglomeration is observed in BaCO_3 while virtually nonexistent in BaSO_4 [10].

Seeding a solution with foreign materials has often been used to induce crystal formation and particle growth. It is usually important for the seed material to have the same crystalline structure as the crystals that are being grown. A common example is using silver iodide to seed rain clouds in an effort to form ice crystals that will fall down as rain [1]. Seeding BaSO₄ particles has not been attempted to a great extent, but it has been found that there exists a seed loading (0.0623 g/L) at which a peak supersaturation ratio exists. Supersaturation ratio is defined as the product of BaSO₄ activity and molar barium ion concentration divided by the thermodynamic solubility product of BaSO₄ [16]. As the supersaturation ratio increases, the rate of nucleation increases which causes a decrease in average particle size [10, 1]. Given this information, the seed concentration at which the peak supersaturation ratio exists should be avoided.

Settling

Particle settling out of suspension occurs in one of four manners: discrete, flocculant, hindered, and compression. These phenomena take place at progressively higher particle concentration and are illustrated in Figure 3.

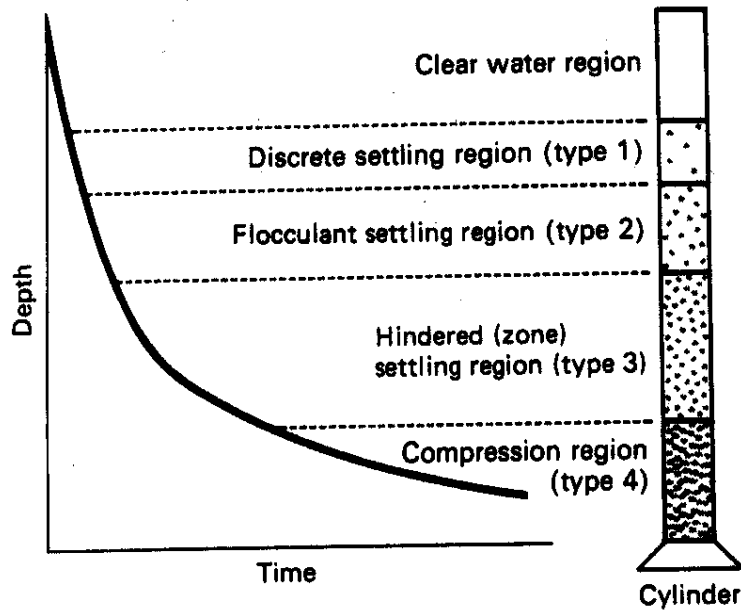


Figure 3: Diagram of the different types of settling phenomena [9].

Discrete settling occurs in dilute suspensions in which the individual particles do not interact with each other. Flocculant settling refers to the sedimentation in which the particles interact to form weak particle-particle bonds. This type of settling is faster than discrete settling because the net particle size is larger than discrete [9].

More concentrated suspensions settle in a manner known as hindered settling. In this method, the particle-particle interactions are strong enough to allow neighboring particles to slow the settling rate of each other. The liquid moves up through the suspension in the interstices of the particles as the particles settle towards the bottom. The particles remain in the same position relative to each other, forming a zone of gradated concentration more concentrated at the bottom and less concentrated at the top. An interface forms above which is clear solution and below which is concentrated solids suspension. Since the particles in the suspension are always at the same position relative to each other, the overall settling rate is slower than discrete and flocculant settling [9].

Compression settling occurs at very high solids concentrations. Any further settling occurs only because of the compressive forces created by the ever increasing weight of particles falling onto the lower layer of particles. Thus, the settling rate due to compression is extremely slow [9].

Experimental

Preparation of Solutions

The Na_2SO_4 and Na_2CO_3 solutions were prepared in the same manner.

Preparation of the BaS solution was complicated because of the reactivity of BaS with oxygen, so a glove bag containing a nitrogen purge was used. At all times when the BaS solid or solution was being used, a constant nitrogen stream was fed to the glove bag and a small opening was left on the front of the glove bag to ensure that no air contaminated the glove bag. Furthermore, nitrogen was bubbled through deionized water inside the glove bag to purge the oxygen from the water used to make the BaS solutions.

A scale accurate to 0.1g was placed inside the glove bag, and a 50mL beaker and parafilm were pre-weighed on another scale accurate to 0.0001g. For 400mL of a 0.100M solution of BaS, 6.774g of solid BaS was needed. On the 0.1g scale inside the glove bag, approximately 6.7 to 6.8g BaS was measured and placed in the 50mL beaker and sealed with parafilm. The beaker, parafilm, and BaS were then weighed on the 0.0001g scale, and the difference was taken to determine the exact amount of BaS solid in the beaker. From this information, the amount of water needed to make a 0.100M solution of BaS was determined, and the nitrogen-purged deionized water was used. The BaS solid and water were poured into a 250mL E-flask and agitated by swirling. At all times, the 0.100M BaS solution was inside the glove bag, and parafilm covered the top to prevent oxygen from contaminating the solution.

Reaction Kinetics

40mL of 0.100M Na_2CO_3 solution was placed in a 100mL beaker and agitated using a magnetic stirrer. 40mL of 0.100M BaS solution was added to the Na_2CO_3 at time zero, and a conductivity probe measured the conductivity of the solution over time. The conductivity was recorded every ten seconds until it became constant at which point it was assumed that the reaction was complete. This same procedure was also carried out using Na_2SO_4 in place of Na_2CO_3 to produce BaSO_4 , and both reactions were carried out at 25°C. The integral method of analysis was used to determine the reaction orders and rate constants.

Reaction Conversion

The overall principle used to determine reaction conversion was to react stoichiometric amounts of BaS and sodium salt (either Na_2SO_4 or Na_2CO_3), weigh the resulting precipitate, and compare with the amount of precipitate that should be theoretically produced. All reactions were performed in the nitrogen-purged glove bag. For the BaS/ Na_2CO_3 system, 40mL of 0.100M BaS solution were reacted with 45mL of 0.100M Na_2CO_3 solution which gave a slight excess of Na_2CO_3 . This excess was necessary to ensure that all BaS was consumed to prevent it from reacting to foul the machine used to measure particle size. The solutions were mixed in a 250mL E-flask and swirled for five minutes.

One VWR 494 filter paper (1 μm pore size) was weighed and placed inside a vacuum filter funnel. The precipitate resulting from the above reaction was poured into the funnel on top of the filter paper which was held down by a ceramic cylinder to keep

precipitate from going around the filter paper. After filtration, the precipitate and filter paper were dried overnight and weighed.

The same procedure was followed for BaS/Na₂SO₄, but 100mL of each solution was used because substantial amounts of precipitate were lost through and around the filter paper for this reaction. At this higher level of product, the amount of precipitate lost through or around the filter compared to the amount captured by the filter is relatively small as opposed to the same ratio using smaller amounts.

Heat of Reaction

Equimolar amounts of BaS and sodium salt solutions were used to determine the heats of reaction. Since a smaller amount of water would theoretically lead to a larger temperature change due to the high heat capacity of water, concentrated solutions were desirable for this experiment. For the reactions, a 1.31M sodium salt solution was mixed with a 0.100M BaS solution. 50mL of BaS solution was poured into a 100mL beaker, and 3.82mL of salt solution was stored in a pipette giving an equal number of moles of each reactant. The BaS solution was placed on a magnetic stirrer, and the initial temperature was measured using a digital thermometer accurate to 0.1°C. The salt solution was added to the BaS solution under agitation, and the final temperature was recorded. This procedure was used for both Na₂CO₃ and Na₂SO₄.

Particle Size

Particle sizes were measured using the Malvern Series 2600 Droplet and Particle Size Analyzer which has a range of 1-1000µm.

Numerous techniques of mixing the BaS and sodium salt solutions were employed in an attempt to maximize the particle size of the precipitates. Common practices in all techniques included the following:

- All reactions were carried out in the nitrogen-purged glove bag to prevent oxidation of BaS.
- A slight excess of sodium salt solution was used to ensure that all BaS was converted to BaSO₄ or BaCO₃; this was done to minimize fouling of the Malvern instrument.
- Precipitate mixtures were very well agitated before being pipetted into the Malvern to ensure a random sample.

The following specific techniques were employed for different experiments to study their effects on the particle size distribution of the precipitate:

- Both the BaS and sodium salt solutions were poured into a flask simultaneously.
- Higher concentrations of each reactant were used.
- One mixture of two parts BaS, one part Na₂CO₃, and one part Na₂SO₄ on a mole basis added simultaneously to a flask was reacted.
- Sodium salt solutions were added slowly to the BaS solution with agitation until all the salt solution was added.
- BaS solution was added slowly to the sodium salt solution with agitation until all the BaS solution was added.
- 0.31g/L of BaSO₄ seed particles were used in BaSO₄ particle size manipulation experiments.

Settling

100mL of the resulting BaSO₄ or BaCO₃ suspensions were well agitated and poured into a 100mL graduated cylinder at time zero. Time values corresponding to the tick marks on the graduated cylinder were recorded as often as possible when the clear liquid-concentrated suspension interface passed. Measurements were taken until either the suspension was completely settled or until one hour had elapsed – whichever happened first.

The effect of time on particle size and zeta potential was studied over the course of eight days to attempt to find reasons why the particle size of the BaCO₃ product decreased over time while the particle size of the BaSO₄ product remained constant. Zeta potential was measured using the Malvern Zetasizer 3000.

Results and Discussion

Reaction Kinetics

Conductivity of solution was the process variable used to measure the change in reactant concentration during reaction. Equimolar 0.100M concentrations of BaS and appropriate sodium salt were added to a beaker in which a conductivity probe was placed. As the reaction proceeded, the ion concentration decreased which caused a reduction in solution conductivity. Since ion concentration is linearly proportional to solution conductivity at low concentrations, the conductivity measurements were normalized by subtracting the minimum conductivity measured from each prior conductivity measurement. Thus, the maximum conductivity observed was at 0.050M BaS and the minimum conductivity observed was at 0.000M BaS i.e. completion (see Reaction Conversion discussion below).

Using this method, the conductivity readings for both reactions were converted into BaS concentrations, and the data are plotted in Figure 4.

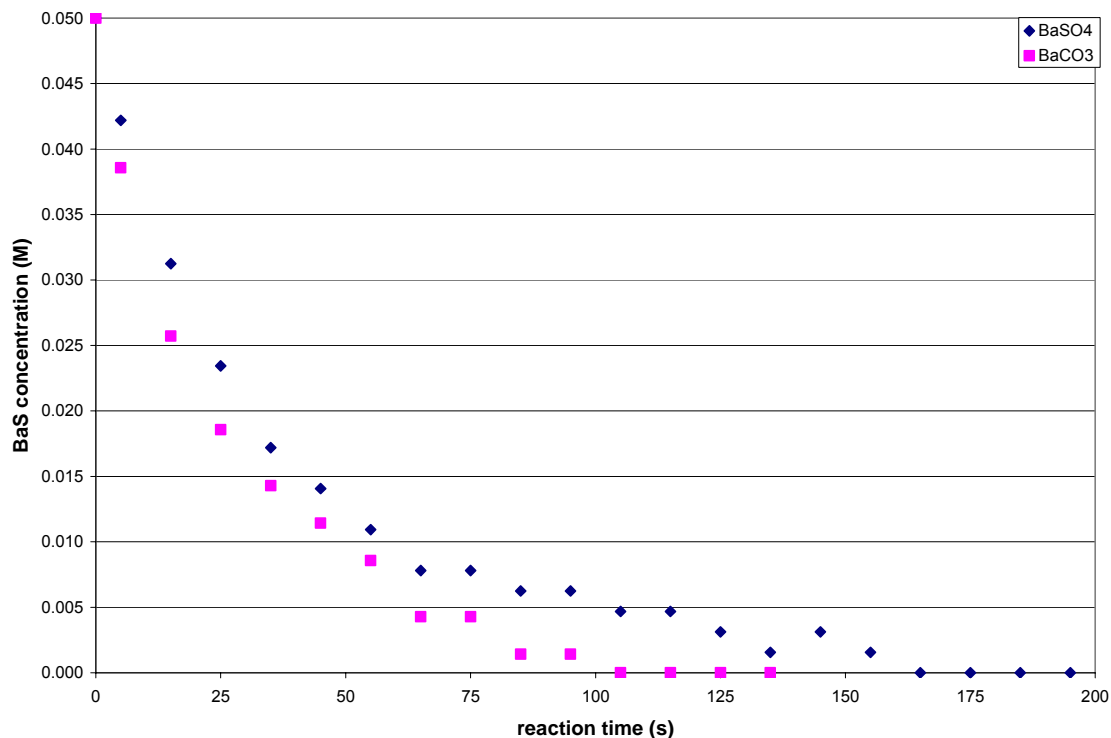


Figure 4: BaS concentration versus reaction time for reactions to form BaSO₄ and BaCO₃ to show the rate of reaction.

The BaCO₃ reaction took less than two minutes to complete while the BaSO₄ reaction took less than three minutes reach completion. To find the rate laws of each reaction, the integral method of analysis was used. It was found that the first order model was the best fit for both reactions as shown in Figure 5. The tabulated reaction order and rate constant values for both reactions are displayed in Table I.

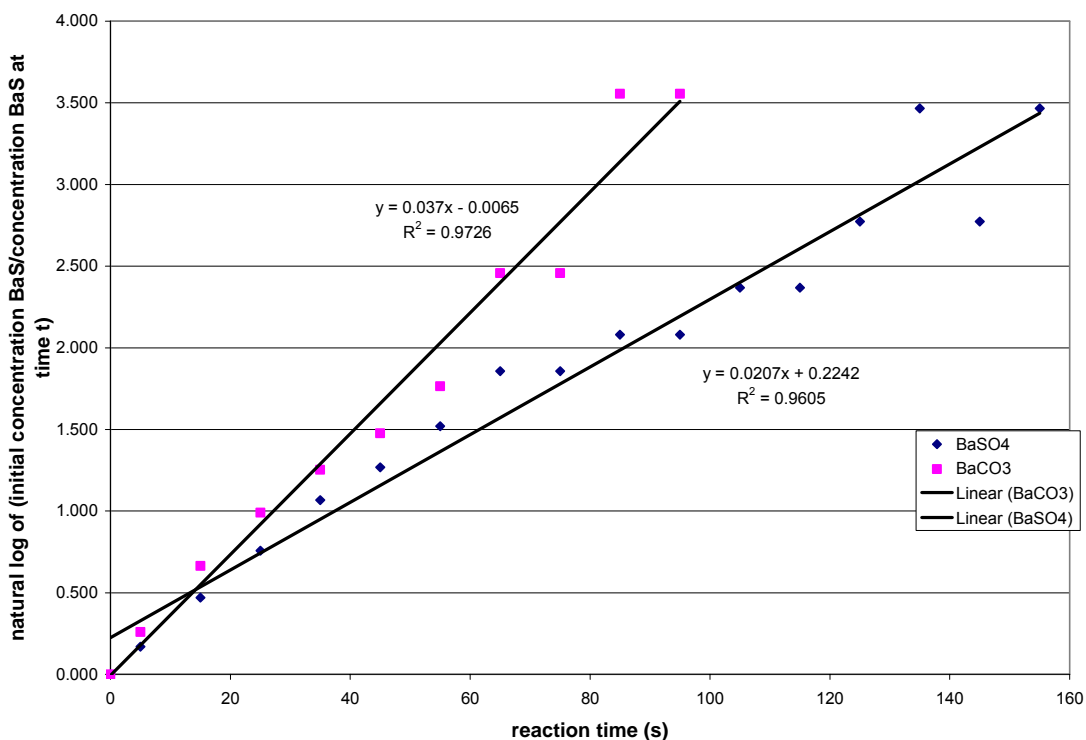


Figure 5: Plot to confirm that both reactions follow first order kinetics.

Table I: Kinetic data for the reactions to form BaSO₄ and BaCO₃ at 25°C.

Product	reaction order	rate constant	rate constant units
BaSO ₄	1	0.037	s ⁻¹
BaCO ₃	1	0.021	s ⁻¹

The conductivity of the solution at the initial stages of the reaction is primarily a function of the ion concentration in solution. However, as the reaction proceeds and more solid particles are generated, the conductivity is then affected by these new particles to a greater extent than was experienced initially. It was found experimentally that the presence of solid particles in a salt solution caused a decrease in the conductivity by as much as 1.5% at these experimental conditions. Thus, the measured conductivity corresponds to a slightly higher ion concentration than was given by the correlation

between conductivity and concentration. This degree of error is not significant, although it should still be noted for future reference.

Future experiments should be performed using the method of excess to determine with respect to which reagents the reactions are first order. Due to the limited supply of BaS available for this study, it is yet unknown whether the reactions are first order with respect to BaS, sodium salt, half order with respect to each, or other combinations. It is only known that the reactions are overall first order.

Reaction Conversion

The attempt to confirm the reaction conversion was performed in duplicate, and the average of the results are displayed in Table II below. These data were obtained for a five minute reaction duration. Conversion is defined as the experimental mass of precipitate formed divided by the expected mass of precipitate.

Table II: Experimental results of attempt to show complete conversion.

Product	average reaction conversion
	%
BaCO ₃	94.6
BaSO ₄	98.7

During the filtering process of BaCO₃, a small amount of solid remained on the ceramic cylinder used to prevent the solution from falling around the filter paper, so the actual conversion is in reality higher than what is reported in Table II. The results for the BaSO₄ conversion were obtained after a second attempt because during the BaSO₄

filtration in the first attempt, it was observed that substantial amounts of BaSO_4 either went through or around the filter paper into the filtrate. Since the extent of reaction appeared to be very small, a second attempt was made using 100mL each of the Na_2SO_4 and BaS solutions. This larger volume minimized error incurred by precipitate either falling through or going around the filter paper by assuming that the quantity of lost precipitate is approximately constant in relation to the amount of solution to be filtered. Also, the level of liquid remaining in the ceramic cylinder dropped very slowly indicating that the filter paper was blinded quickly by the BaSO_4 . These results gave the first indication that the particle size of BaSO_4 is smaller than that of BaCO_3 .

Heat of Reaction

Data for heats of reaction for reactions in this project are available in thermodynamic tables. Experiments were run nevertheless to determine if there were any unexpected heat of mixing effects that would be greatly exaggerated on an industrial scale. The first runs used a 0.100M BaS solution and more concentrated 1.31M sodium salt solutions; however, the volumes of solutions used were such that the reaction mixture was equimolar with respect to the reactants. Theoretical heat of reaction data were determined using heats of formation data found in literature [7]. All theoretical and experimental results are displayed in Table III below.

Table III: Heat of formation data obtained for dilute BaS solution and concentrated sodium salt solution.

		BaS	Na ₂ SO ₄		BaS	Na ₂ CO ₃	
concentration	M	0.100	1.31		0.100	1.31	
volume	mL	50	3.82		39	2.98	
active moles	mol	0.005			0.0039		
T_i	°C	24.0			24.0		
T_f	°C	24.3			24.1		
ΔT	°C	0.3		margin of error	0.1		margin of error
ΔH_{f-experimental}	kJ	-0.0676		+/- 0.203	-0.0176		+/- 0.0158
ΔH_{f-theoretical}	kJ	-0.0768			-0.0496		
ΔH_{f-experimental}	kJ/mol	-13.5		+/- 4.06	-4.51		+/- 4.051
ΔH_{f-theoretical}	kJ/mol	-15.4			-12.7		

A large margin of error is inherent in all of the results because the digital temperature probe was accurate to 0.1°C. As a result, temperatures ranging from 23.95°C to 24.04°C would all register as 24.0°C. Considering the theoretical heats of reaction, it was determined that the expected adiabatic temperature rise is 0.34°C for the BaSO₄ reaction and 0.28°C for the BaCO₃ reaction. The BaSO₄ value is within the margin of error for the temperature probe while the BaCO₃ value is out of the error range. A possible explanation for this is that the beaker in which these tests were performed was not insulated, so there was the possibility of heat loss to the ambient. Since the BaCO₃ reaction involved a smaller amount of solution, the same amount of heat loss from both mixtures would affect the BaCO₃ mixture to a greater extent.

In either case, all heat effects for these reactions (heat of mixing and heat of reaction) are not exceedingly large and, therefore, should not cause problems in an industrial application.

Particle Size

Attempted manipulation of the particle sizes of the precipitated BaCO_3 and BaSO_4 involved simultaneously pouring the appropriate 0.100M sodium salt and BaS solutions into a flask under agitation (simultaneous addition) as well as using concentrated sodium salt and BaS solutions (concentrated reactants). In the concentrated reactants runs, the BaS solutions are 0.292M and the sodium salt solutions are 1.31M. These concentrations are just below the respective solubility limits of each compound. The results for each compound are presented below in Figures 6 and 7 along with a run ($\text{BaSO}_4/\text{BaCO}_3$ combination) in which 2 parts 0.100M Na_2SO_4 and Na_2CO_3 were added to one part 0.100M BaS all on a molar basis. $D_{0.5}$ is the linear average particle size, and $D_{0.1}$ and $D_{0.9}$ represent the lower and upper particle sizes, respectively, in between which are 80% of the particles.

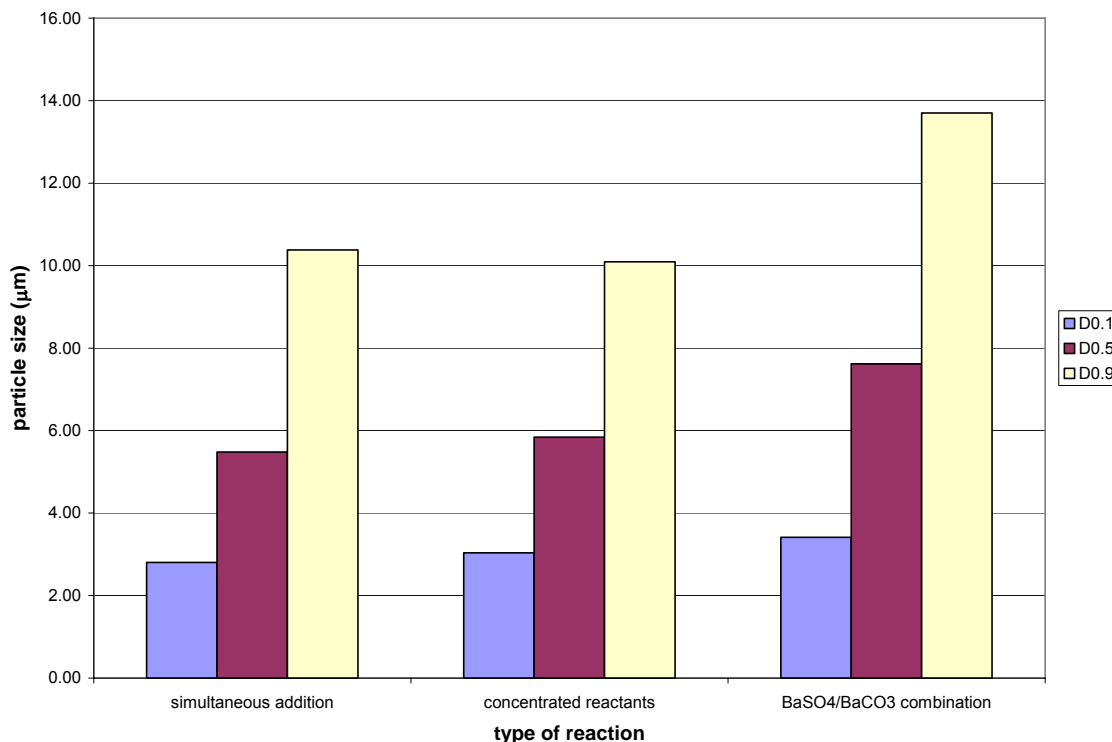


Figure 6: Particle size distribution data comparison of BaSO_4 precipitates.

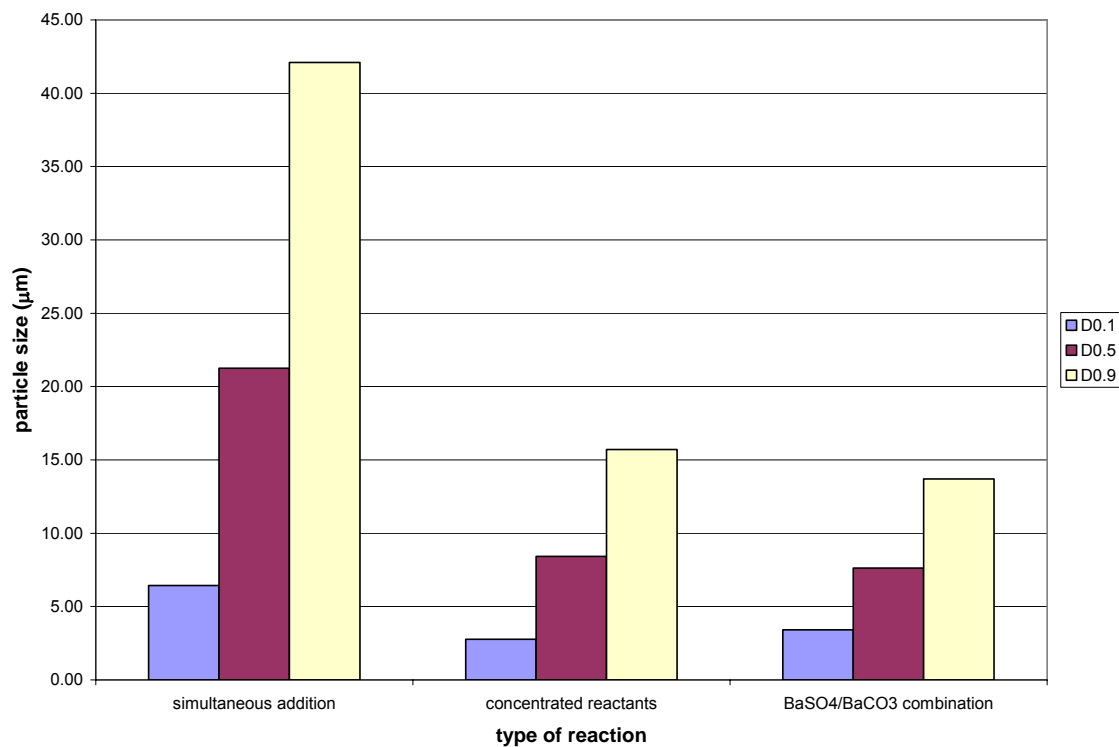


Figure 7: Particle size distribution data comparison of $BaCO_3$ precipitates.

Several observations can be made at this point. It was reported in the literature that higher ion concentrations would lead to the favorable condition of a faster crystal growth rate and a slower nucleation rate as long as the concentration was not so high as to cause the ions to interfere with particle adhesion to crystal surfaces. In other words, fewer particles yield larger particle sizes for a given total concentration. For $BaSO_4$, the concentrated reactants run gave approximately the same particle size distribution as the relatively dilute simultaneous addition run, indicating that neither the crystal growth rate nor nucleation rate was affected by the higher concentration. However, for $BaCO_3$ in Figure 7, concentrated reactants unexpectedly resulted in a much lower particle size than the simultaneous addition. This is due to the fact that $BaCO_3$ forms agglomerates, but the

higher concentrations of ions in solution interfered with the formation of the agglomerates, so the observed particle size was smaller.

As expected, the combination of BaSO_4 and BaCO_3 had a larger particle size than the BaSO_4 but smaller than BaCO_3 . However, the average particle size of the combination was only about $4\mu\text{m}$ greater than the BaSO_4 particle size and about $7\mu\text{m}$ less than the BaCO_3 particle size. The BaSO_4 particles that formed interfered with the agglomeration of BaCO_3 in that the BaCO_3 particles did not adhere to each other due to the presence of BaSO_4 or the adhesion did occur but in a weakened state. Thus, the shear forces created by the stirring rod were greater than the attractive forces between BaCO_3 particles. In either case, BaCO_3 did not form as large agglomerates as it did in the absence of BaSO_4 .

Neither precipitate gave a normal distribution although the BaSO_4 is much closer to being normal as BaCO_3 shows a strong negative skew (see the particle size distributions in the Appendix). The larger particle size of BaCO_3 was found to be due to agglomeration of smaller particles which does not occur with BaSO_4 .

In an effort to increase particle size of BaSO_4 , an experiment was performed using seed particles of BaSO_4 to provide a surface on which crystal growth can occur at the very beginning of the reaction. The seed was always added to the solution in the beaker initially, and for one of the seeded runs BaS was in the beaker initially. For the other seeded run, Na_2SO_4 was in the beaker initially with the BaSO_4 seed. Seed concentration was 0.31g/L as was found in the literature [16], and its particle size distribution is in Figure 8. The seed used was BaSO_4 solid ordered from a chemical supplier.

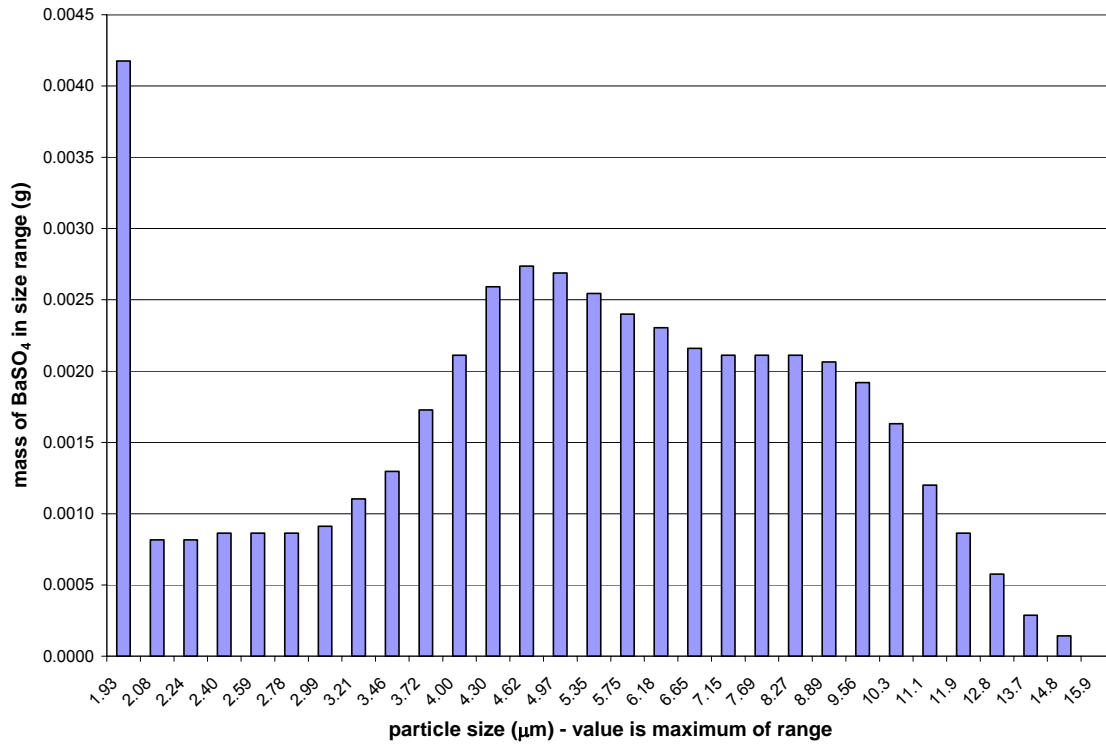


Figure 8: Mass particle size distribution for BaSO₄ seed particles.

The results from these tests are illustrated in Figure 9, and the average particle sizes are displayed in Table IV.

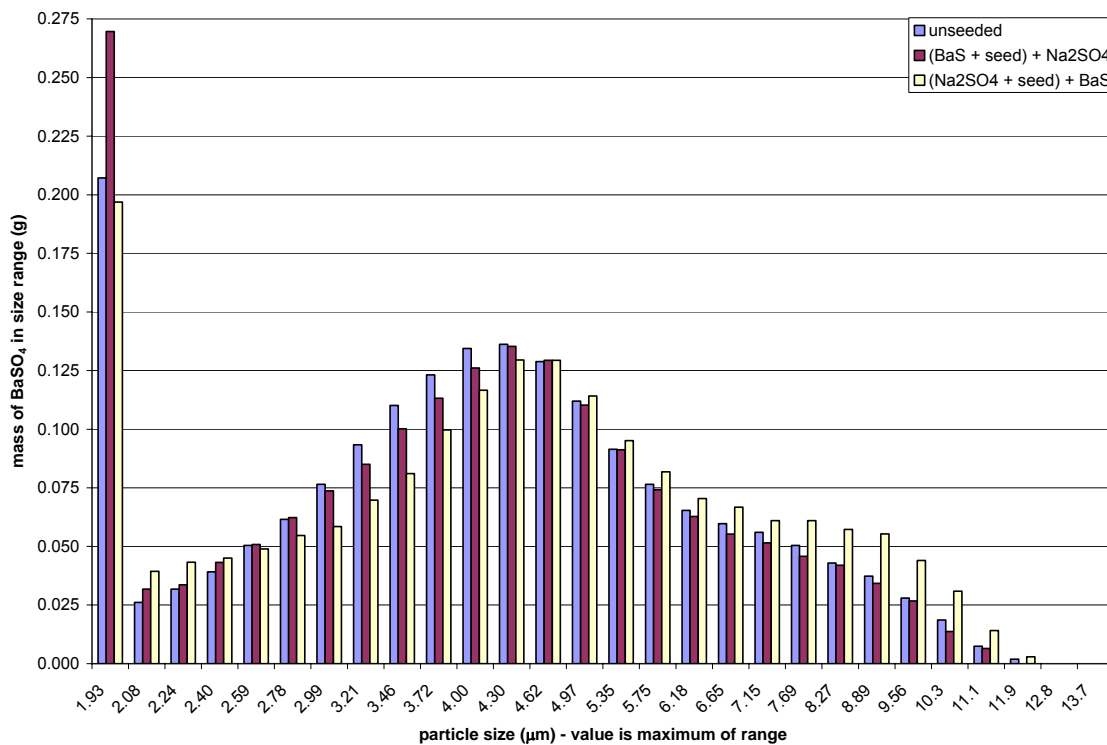


Figure 9: Mass particle size distributions of seeded BaSO₄ products only (seed has been subtracted from the distribution) in comparison to unseeded BaSO₄.

Table IV: Linear average particle sizes of unseeded and seeded BaSO₄ products.

Run	linear average particle size
	µm
unseeded	3.96
(BaS + seed) + Na ₂ SO ₄	3.89
(Na ₂ SO ₄ + seed) + BaS	4.20

From these data, it can be seen that seeding did not appreciably increase the particle size of BaSO₄. In fact, for the reaction in which BaS and seed were present in the beaker initially, the measurement obtained shows a decrease in particle size, but this difference is within the approximate reproducibility range of the Malvern instrument. Due to having only a small amount of BaS reactant to use, it was not possible to complete

multiple runs using different seed concentrations or particle sizes, so the seeding concept should not be abandoned based solely on the data obtained in this study.

It was observed that particle size measurements of BaCO_3 taken about a day later than the initial measurements were substantially smaller than the initial measurements. Formal data are presented in Figure 10. The order of addition of reactants was studied as well, and the results are also combined into Figure 10. Runs 1 and 3 were performed with BaS in a beaker with agitation and the appropriate sodium salt poured slowly into the beaker. Runs 2 and 4 were performed with the sodium salt in a beaker with agitation and BaS poured slowly into the beaker.

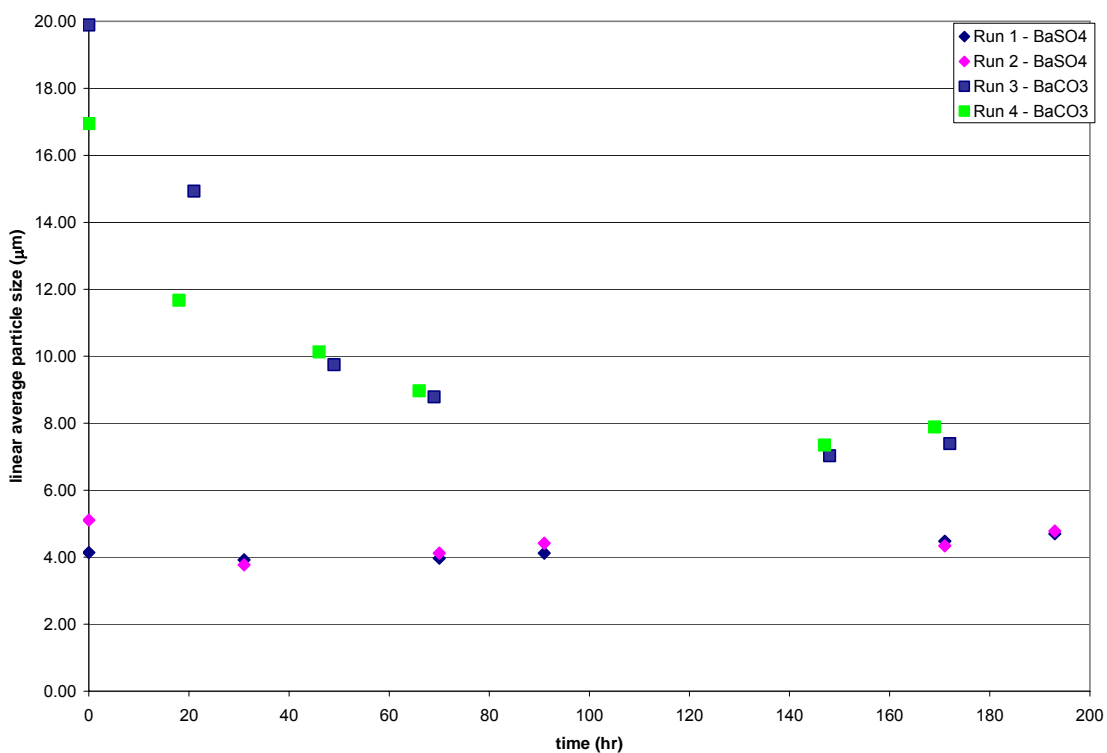


Figure 10: Linear average particle sizes of BaSO_4 and BaCO_3 over time.

As is obvious in Figure 10, the order of addition of reactants is unimportant for BaSO_4 while adding Na_2CO_3 slowly to BaS to produce BaCO_3 is slightly preferable to

the opposite order of addition. Also, the trend of decreasing particle size of BaCO_3 over time is easily discernable, but this phenomenon is nonexistent for BaSO_4 . This is due to the disagglomeration of BaCO_3 over time, although the samples were not agitated or otherwise sheared between measurements which is the main cause of disagglomeration. For industrial applications, this behavior should not be a problem because it is unlikely that BaCO_3 would remain stagnant for the length of time that it takes for non-agitation disagglomeration to occur.

In an effort to understand this behavior and perhaps to determine if it was due to surface chemistry, measurements of zeta potential were performed on each sample over time. These data are illustrated in Figures 11 and 12 below. As discussed earlier, zeta potential is the potential between the bulk solution and the electric double layer surrounding a particle.

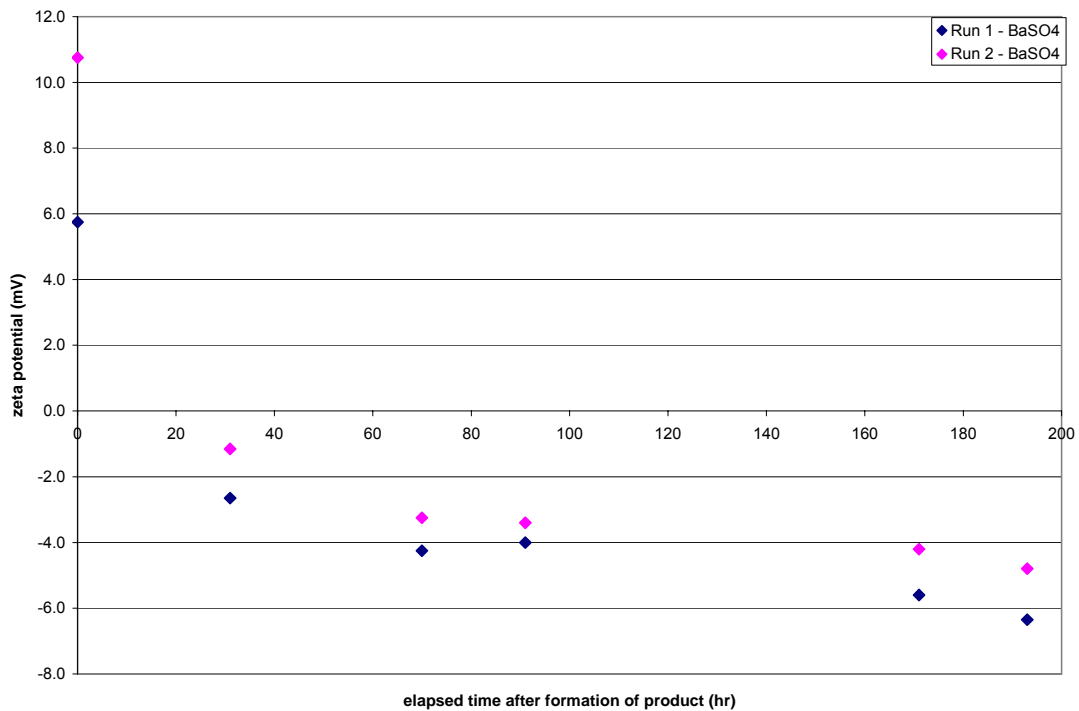


Figure 11: Zeta potentials of BaSO_4 over time.

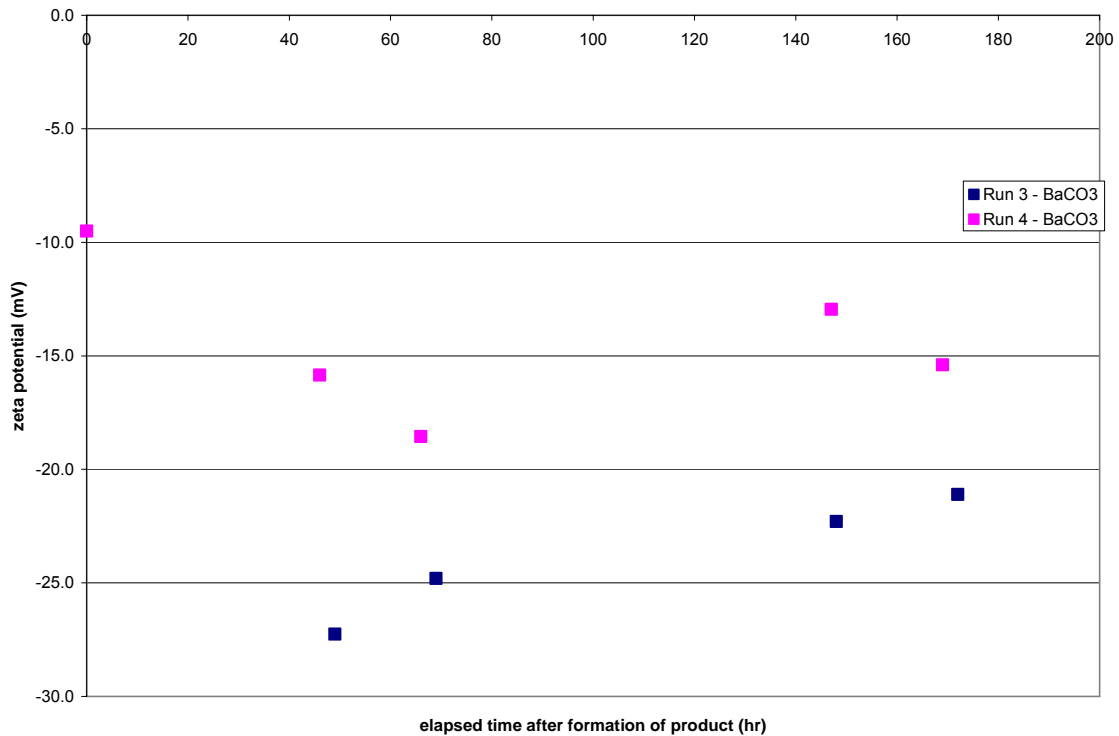


Figure 12: Zeta potentials of BaCO₃ over time.

A major caveat accompanies these data. The positive zeta potentials indicating a positive surface charge obtained for BaSO₄ at zero hours seems out of place because every other point for both BaSO₄ and BaCO₃ show negative zeta potentials. These zeta potentials were obtained a day before the first ones were obtained for BaCO₃, so it is likely that the Zetasizer was malfunctioning when the first BaSO₄ readings were taken. However, it was impossible to know this at the time that the samples were analyzed.

Zeta potentials of BaCO₃ are much more negative than those of BaSO₄ indicating that the electric double layer surrounding the BaCO₃ particles is larger than that of BaSO₄. Theoretically, this indicates that the particle-particle repulsion of BaCO₃ is strong and, therefore, BaCO₃ particles should resist colliding and definitely not form agglomerates. However, as has been discussed before, BaCO₃ does form agglomerates,

so it must be concluded that for BaCO_3 , the repulsive force induced by the electric double layer is much smaller than the attractive force pulling the particles together. BaSO_4 behaves in the exact opposite manner in that it has a relatively small zeta potential indicating a small electric double layer, but the relatively weak repulsion force is still strong enough to dominate the attractive force. No explanation could be found in the literature for the fact that BaCO_3 exhibited agglomeration while BaSO_4 did not.

Settling

BaSO_4 and BaCO_3 suspensions were tested in a graduated cylinder to determine the relative settling rates. Each suspension was the result of mixtures of 0.100M reactant solutions, so the solid concentrations were also 0.100M. However, due to the differing molecular weights of BaSO_4 and BaCO_3 , the mass concentrations of each suspension were slightly different – e.g. 23.3g/L for BaSO_4 and 19.7g/L for BaCO_3 . The results for the BaSO_4 and BaCO_3 settling rate experiments are displayed in Figures 13 and 14, respectively. BaSO_4 settled quickly, but the BaCO_3 settling experiment was stopped after one hour due to the extremely slow settling rate. This behavior is explained later.

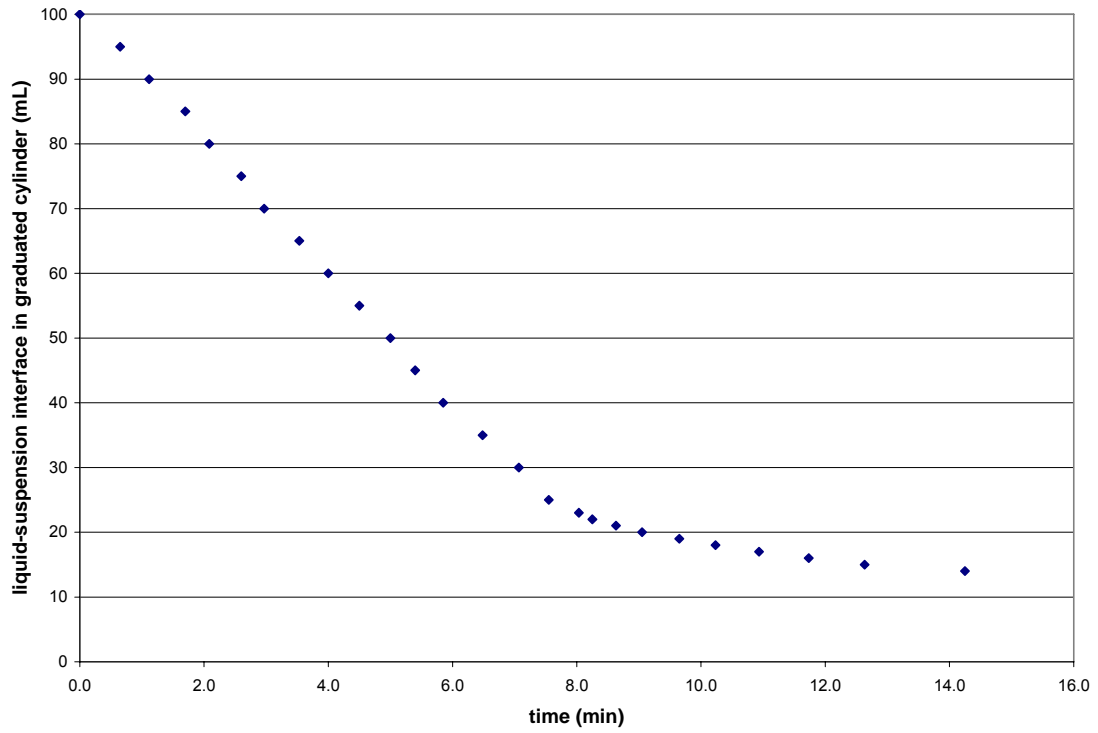


Figure 13: Particle interface level as a function of settling time in a graduated cylinder for $BaSO_4$.

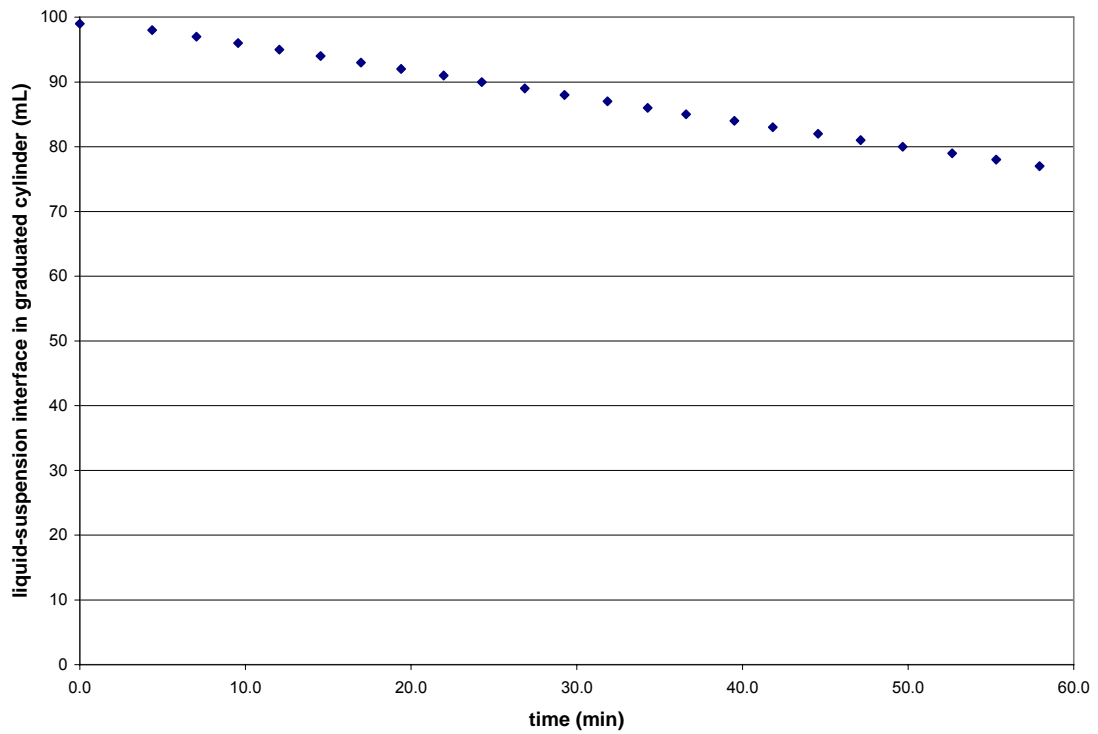


Figure 14: Particle interface level as a function of settling time in a graduated cylinder for BaCO₃.

The settling curve for BaSO₄ is very similar to the profile in Figure 3 in the Literature Review detailing the four types of settling phenomena. However, it should be noted that as the particles settled, it was very difficult to discern an interface between relatively clear and concentrated portions of the suspension. In other words, discrete and flocculant settling dominated initially, and compression settling occurred at the bottom of the cylinder. Hindered settling was virtually nonexistent because the interface was also virtually nonexistent. This result supports the notion that there is very little particle-particle interaction between BaSO₄ particles.

BaCO₃ settled very slowly as can be seen in Figure 14. The interface between the clear and concentrated portions of the suspension was easily recognized as it moved down the cylinder. In stark contrast to BaSO₄, no discrete or flocculant settling regions could be distinguished in the BaCO₃ suspension, but the hindered and compression regions were evident. Since hindered settling is so slow, all the discrete and flocculant settling was complete from the top of the liquid level down to the interface almost immediately. Again, this result verifies the presence of particle-particle interactions between BaCO₃ particles.

The hindered settling characteristic of the particles remaining at the same position relative to each other was also very evident. The agglomerates that formed proved to be extremely rigid in that there was very little disruption in the appearance of the suspension as it settled. Most of the liquid that traveled up the cylinder as the particles settled moved through the spaces in between the agglomerates. However, since the agglomerates were so large and very possibly interacting with each other forming “macroagglomerates,” it

was very difficult for the liquid to move up the cylinder which is why the settling rate was so slow.

Occasionally, some small convective currents were noticed in the BaCO_3 hindered settling region near the bottom. These currents were not due to heating since the system remained at uniform temperature; rather, they were due to partial collapses of macroagglomerates near the compression zone. Because of these collapses, liquid was displaced much more rapidly than under normal settling conditions. However, the convective currents lasted no more than a few seconds because they ran out of momentum and thus lacked sufficient force to disrupt macroagglomerates that were farther away from the compression zone.

Another result of note is that even though BaSO_4 was more concentrated in suspension than BaCO_3 (23.3g/L for BaSO_4 as compared 19.7g/L for BaCO_3), the BaSO_4 still did not exhibit strong enough particle-particle interactions to affect settling.

Conclusions

The reaction of BaS and Na₂SO₄ to form BaSO₄ was found to be overall first order with a kinetic rate constant of 0.037 s⁻¹, and the reaction of BaS and Na₂CO₃ to form BaCO₃ was found to be overall first order with a kinetic rate constant of 0.021 s⁻¹. Both rate constants are valid only at 25°C. The disruption of solution conductivity due to solid particle interference did not have a significant effect on the concentration-conductivity correlation. Both reactions were determined to go to at least 94% completion, but it can be hypothesized that they are near 100% efficient assuming that the remaining conversion comes from the mass of precipitate that circumvented the filter paper.

Neither reaction showed any unexpected or significant heat of reaction or heat of mixing. The reaction to form BaSO₄ is slightly more exothermic than that of BaCO₃ (-15.4 kJ/mol as compared to -12.7 kJ/mol, respectively). For the conditions of this experiment, the expected adiabatic temperature rise was 0.34°C for the formation of BaSO₄ and 0.28°C for the formation of BaCO₃.

BaSO₄ particle sizes averaged anywhere from just under 4µm to just over 5µm and seeding the initial solution with BaSO₄ particles had no apparent effect on particle size. Also, the average particle size of BaSO₄ did not change over time. BaCO₃ particle sizes ranged from approximately 21µm initially to down to 7µm after several days because the BaCO₃ agglomerates broke down over time even with no agitation. BaCO₃ initially formed agglomerates while BaSO₄ did not, and the reason for this behavior could not be found experimentally or in the literature. Concentrated reactant solutions used to

form BaSO_4 and BaCO_3 produced smaller particle sizes than the 0.100M solutions used because the rate of nucleation was much higher for concentrated solutions, so the crystals did not have a chance to grow before the reactants were consumed. BaSO_4 and BaCO_3 formed simultaneously in one mixture produced a particle size of $7.6\mu\text{m}$ which was closer to the average BaSO_4 particle size than that of BaCO_3 .

BaSO_4 exhibited discrete and flocculant settling characteristics because it did not form agglomerates. The bulk of the particles settled quickly, although there was still a significant mass of particles remaining in suspension. BaCO_3 exhibited hindered and compressive settling because it did form agglomerates due to strong particle-particle interactions. It settled very slowly, but the liquid above the suspension interface was very clear indicating that virtually all of the particles had settled.

Recommendations for Future Work

- More extensive study of kinetics is required for both reactions to find the activation energies and to determine individual orders which result in overall first order.
- Perform the reactions in this study in combination with barium hydroxide to study the selectivity of the sodium species.
- Perform experiments to determine the critical agitation and reactant concentration that will give a maximum particle size of BaSO_4 . Also, determining the reason why BaCO_3 forms agglomerates while BaSO_4 does not is necessary to force BaSO_4 to agglomerate.
- More extensive testing on the effect of seed particles on particle size is required as this study did not go into great detail on this subject.
- To aid in settling of the particles out of suspension, organic additives/surfactants should be considered and tested.

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