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Direct Causticizing of Sodium Carbonate with Manganese Oxide

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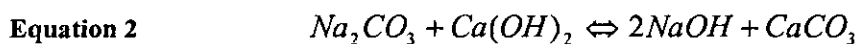
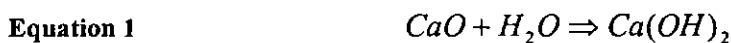
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Abstract

Manganese oxide, as Mn_3O_4 , was investigated as a direct causticizing agent. The reaction between Mn_3O_4 and Na_2CO_3 was found to occur with 1:1 stoichiometry. The reaction mechanism is well described by the Ginstling-Brounshtein product-layer diffusion controlled model. In the solid state, from 650 – 850°C, the activation energy is 206 kJ/mol; with molten Na_2CO_3 , from 850 – 950°C, the activation energy is 174 kJ/mol. An increase in the Mn_3O_4 particle size reduces the reaction rate, while excess Mn_3O_4 in the reaction mixture increases the rate of Na_2CO_3 conversion. Hydrolysis of the direct causticizing product forms a caustic solution, with neither the direct causticizing nor hydrolysis reactions being equilibrium-limited. Na_2S has a negative impact on the direct causticizing reaction in that the Na_2S is oxidized to Na_2SO_4 while the Mn_3O_4 is reduced to MnO .

Introduction

One goal of pulp mill chemical recovery is to convert Na_2CO_3 into NaOH for reuse in the digester. The traditional CaO -based chemical recovery process is represented by the following chemical equations.



The reaction in Equation 2 is an equilibrium-limited reaction. In practice, the conversion of sodium carbonate to sodium hydroxide ranges from 80 to 90%, depending on white liquor total titratable alkali[1]. The remaining unconverted sodium carbonate is part of what is known as deadload in the Kraft liquor cycle. The sodium carbonate does not participate in the pulping reaction and is detrimental because additional energy is

needed to heat it and evaporate the water accompanying it during the processes of pulping, evaporation, and combustion. A process that reaches higher efficiencies in the conversion of sodium carbonate to sodium hydroxide would improve both capacity and energy efficiency.

Alternative methods for converting sodium carbonate to sodium hydroxide have been known for many years[2,3]. In the pulp and paper industry, the Direct Alkali Regeneration System (DARS) has been commercialized in Tasmania for use with the soda-anthraquinone pulping process[4,5]. In this system, sodium carbonate reacts with iron oxide at high temperatures in a fluidized-bed reactor. The resulting product, sodium ferrite, is subsequently dissolved in water and undergoes a hydrolysis reaction to form sodium hydroxide and iron oxide. Unfortunately, the iron oxide-based direct causticizing system does not work with kraft pulping liquors. If sulfides are added to the DARS process, they undergo a negative side reaction with the iron oxide to produce stable iron sulfides[5].

Other metal oxides have been identified as possible direct causticizing agents for use with kraft recovery systems. Titanium dioxide is an acceptable compound that does not react unfavorably with sulfur components[6,7]. The mechanism of reaction and kinetics for the TiO_2 system have been well described in the literature. TiO_2 has solid potential for use as a direct causticizing agent with soda and kraft liquors, particularly when combined with gasification. A drawback to TiO_2 -based direct causticizing is the reaction stoichiometry. Upon hydrolysis of the reaction product, one sodium oxide remains associated with three TiO_2 molecules. This 1:3 complex is the actual direct causticizing agent. The reaction of Na_2CO_3 with the 1:3 complex yields a 4:5 complex

that then undergoes hydrolysis. Even though high causticizing efficiencies are obtained, there is a deadload of Na_2O and TiO_2 that is not fully utilized. The ideal situation would be a metal oxide that undergoes complete hydrolysis and is able to complex with one or more Na_2O species.

A Canadian Patent describes a direct causticizing process for soda or kraft chemical recovery using MnO_2 as the preferred causticizing agent[8]. MnO_2 was selected as the direct causticizing agent because it does not readily form the metallic sulfide, MnS [8]. There was no experimental work supporting the claims in the patent.

Giovanoli investigated the thermal reduction of MnO_2 and found that it was reduced to Mn_2O_3 in the temperature range of 500 to 700°C[9]. Further heating leads to the formation of Mn_3O_4 between 900 and 950°C. Mn_3O_4 was stable from room temperature to 1025°C. This thermal reduction suggests that Mn_3O_4 would be the preferred direct causticizing agent.

The goal of this investigation was to study the direct causticizing reaction between sodium carbonate and Mn_3O_4 . Little was known about reaction stoichiometry, mechanisms, and kinetics of this system. In addition, for application to a kraft system, the influence of sodium sulfide on the reaction was also to be investigated.

Experimental

The kinetics of the direct causticizing reaction with Mn_3O_4 were investigated under isothermal conditions. The reactants were swept with nitrogen at a rate of 1 standard liter per minute (SLPM) to remove the CO_2 , allowing continuous analysis of the reaction progress. A horizontal muffle furnace, 30.5 cm in length with a 5.1-cm cylindrical bore, was used to heat the reactants. The furnace had an alumina retort that housed a 1.9-cm-diameter stainless steel tube that was used as the reaction chamber. A

2.6-cm³ alumina boat was connected to a plunger system that allowed rapid insertion of the reactants into the core of the furnace. A schematic of the reactor is shown in Figure 1. The nitrogen purge was directed to infrared CO₂ detectors. The data acquisition integrated the CO₂ concentration and flow rate signals to yield the total CO₂ evolved versus time. This was converted to conversion versus time for kinetic analysis. After completion of the direct causticizing reaction, the weight loss was determined and a fraction of the material was analyzed with x-ray diffraction (XRD) and scanning electron microscopy (SEM) for product identification and characterization. Additional reaction product was hydrolyzed in boiled, deionized water at 90°C for 5 hours under a nitrogen purge. Following hydrolysis, the slurry was vacuum-filtered onto a 4.7-cm PTFE membrane filter with 0.2µm openings. The solid hydrolysis product was also analyzed with XRD and SEM. The aqueous component was titrated with a Mettler DL70ES Auto Titrator to determine NaOH, Na₂CO₃, and Na₂S concentrations. Method 2320, from “Standard Methods for the Examination of Water and Wastewater”, was used for the determination of alkalinity for the sulfur-free analysis[10]. For the sulfur-containing filtrates, the “ABC method” from the Scandinavian Pulp, Paper and Board Testing Committee, SCAN-N 30:85, was used. The experimental conditions for the direct causticizing reaction are:

Temperature: 650 - 950°C

Mn₃O₄ equivalent diameter: 23µm, 104µm, 227µm

Mn₃O₄:Na₂CO₃ initial molar ratio: 1.0, 2.0, 3.0

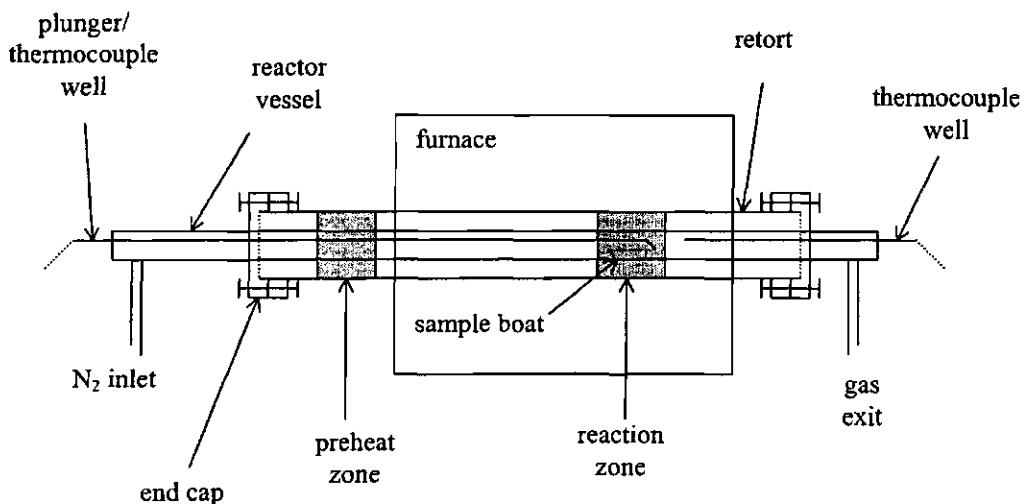


Figure 1. Schematic of reactor used for isothermal experiments.

Sodium carbonate from Mallinckrodt (Analytical Reagent 99.9%) was used. It had a volume mean particle size of $91\mu\text{m}$. Before use, it was dried in a nitrogen-purged oven at 290°C to remove any bound water. The dried material was stored in a dessicator when not in use.

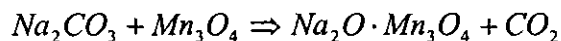
Mn_3O_4 was prepared by the thermal reduction of Baker MnO_2 (Reagent Grade 99.99% < $325\mu\text{m}$). The MnO_2 was placed in an open-top alumina crucible and heated in air at 1075°C for 2 hours. The resulting material was analyzed with XRD to confirm the conversion to Mn_3O_4 . The Mn_3O_4 was mechanically separated with 20.3-cm-diameter stainless steel sieves. Two fractions were retained: $212\text{--}250\mu\text{m}$ and $90\text{--}125\mu\text{m}$. A third fraction was obtained by grinding Mn_3O_4 of $<90\mu\text{m}$ diameter with a mortar and pestle. The material was sieved with the $<38\mu\text{m}$ fraction being saved. The resulting volume mean equivalent diameters were 227, 104, and $23\mu\text{m}$.

Sodium sulfide as $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ fused flakes was supplied by EM Science. The flakes were ground into a fine powder with a mortar and pestle and stored in a dessicator.

The nitrogen used as the purge gas was supplied by Holox. It was Ultra-High-Purity grade with a purity of 99.999%. Air Products supplied calibrated standards of CO_2 in nitrogen at 1799ppm and 9.98% for the IR analyzer calibration.

Results and Discussion

Prior to the kinetic experiments, the stoichiometry of the reaction was determined. A series of experiments with different $\text{Mn}_3\text{O}_4\text{:Na}_2\text{CO}_3$ initial molar ratios was performed at 700, 800, and 900°C. The experiments were run for 24, 12, and 1 hours respectively to ensure complete conversion of the reactants. The total CO_2 evolved and weight loss were used to determine Na_2CO_3 conversions based on the following assumed reaction.



A plot of Na_2CO_3 conversion versus the initial molar ratio of reactants is shown in Figure 2. The dashed line in Figure 2 represents the theoretical conversion for 1:1 stoichiometry. When there is an excess of Na_2CO_3 present in the reaction mixture, for $\text{Mn}_3\text{O}_4\text{:Na}_2\text{CO}_3$ less than 1, the Na_2CO_3 conversion approaches the theoretical maximum based on 1:1 reaction stoichiometry. If more Na_2CO_3 were able to react, higher weight losses would have been recorded. For initial molar ratios greater than 1:1, the limiting reactant is Na_2CO_3 , resulting in weight loss equivalent to 100% Na_2CO_3 conversion. The same stoichiometry was observed for the three temperatures.

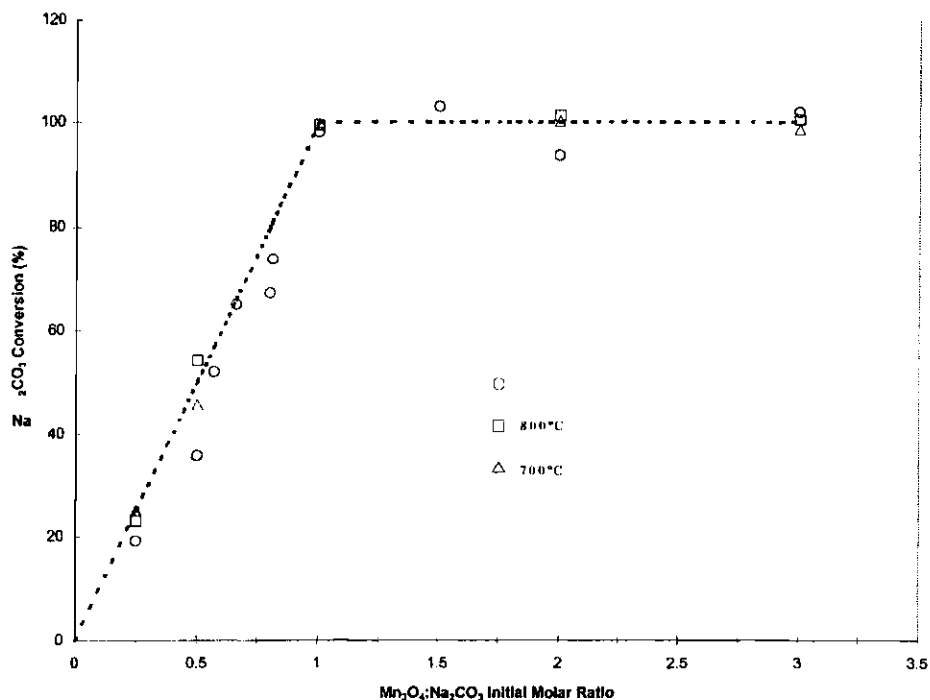


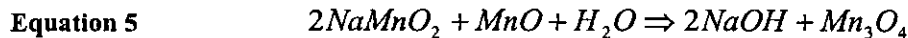
Figure 2. Na₂CO₃ conversion versus Mn₃O₄:Na₂CO₃ initial molar ratio at 700, 800, and 900°C.

XRD analysis of the reaction product did not specifically indicate Na₂O · Mn₃O₄. The identified species were NaMnO₂ and MnO. This suggests that the direct causticizing reaction is



Mn₃O₄ is a mixed oxidation state compound, comprised of Mn⁺² and Mn⁺³ manganese. It can be considered Mn₂O₃ + MnO. The Mn⁺³ manganese appears to be more reactive than the Mn⁺². This results in the formation of NaMnO₂, presumably in solid solution with MnO.

The air-dried solid product following hydrolysis was analyzed with XRD and found to be Mn₃O₄. This suggests that the hydrolysis and drying step are represented by the following mechanism.



The reaction progress between Mn_3O_4 and Na_2CO_3 was monitored by CO_2 evolution. Conversion versus time data were calculated from the initial amounts and stoichiometry of reactants. A plot of typical CO_2 concentration and conversion versus time is shown in Figure 3.

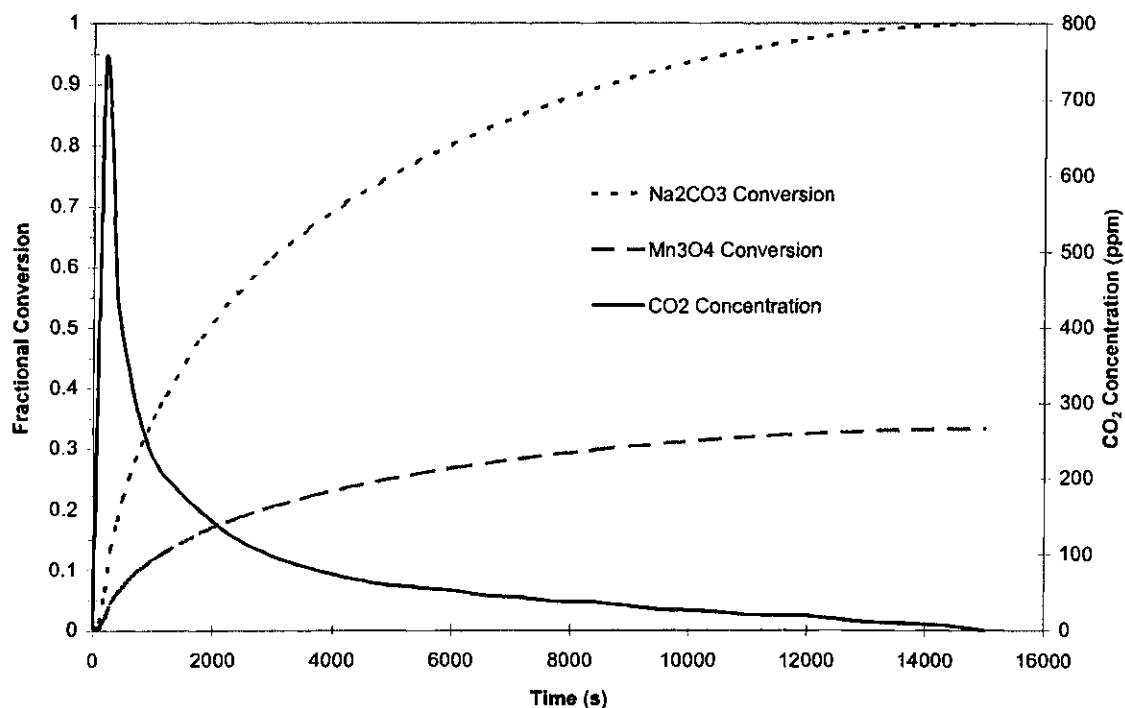


Figure 3. CO_2 concentration and conversion versus time. 827°C , $23\mu\text{m Mn}_3\text{O}_4$, $\text{Mn}_3\text{O}_4:\text{Na}_2\text{CO}_3 = 3:1$.

The conversion versus time data were found to be in good agreement with the Ginstling-Brounshtein product-layer diffusion controlled model. This model was originally developed for the reaction between spherical particles in the solid state. The model assumes that the species with lower melting point, Na_2CO_3 , rapidly diffuses to cover the reacting particle, Mn_3O_4 , with a continuous layer. The Na_2CO_3 reacts with the

Mn_3O_4 to form a product layer. In order for the reaction to proceed, the Na_2CO_3 must diffuse through the product layer. The reaction at the interface is assumed to occur at a much faster rate than the diffusion, implying that the concentration of Na_2CO_3 at the reaction interface is zero.

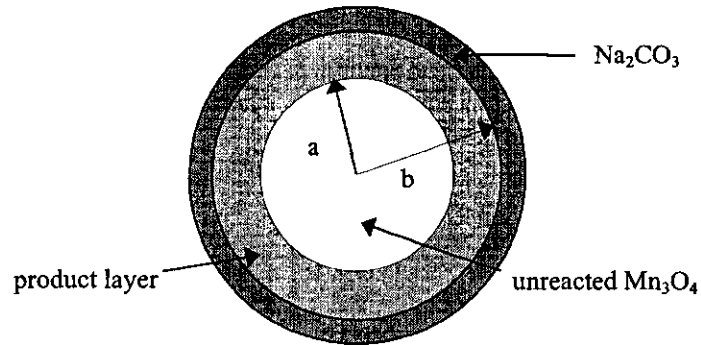


Figure 4. Schematic of product-layer diffusion controlled model in spherical particles.

The concentration of Na_2CO_3 at the surface of the particle, C_0 , is equivalent to its molar volume. The steady-state solution for diffusion through a spherical shell of radii b and a is

Equation 6
$$C(r) = \frac{bC_0(r-a)}{r(b-a)}.$$

The rate of flow of material through the shell, dM/dt , is

Equation 7
$$\frac{dM}{dt} = -4\pi a^2 D \left(\frac{\partial C}{\partial r} \right)_{r=a} = 4\pi D C_0 a b / (b-a).$$

D represents the diffusivity of Na_2CO_3 through the product layer. The above expression was obtained assuming a constant value for a . Ginstling and Brounshtein used a quasi-stationary-state approximation to allow a to vary with t . [11] Therefore,

Equation 8
$$\frac{dM_t}{da} = -4\pi a^2 / V_m$$

and

Equation 9
$$da / dt = -DC_0 V_m b / a(b - a).$$

V_m is the volume of product containing 1 mole of the diffusing Na_2CO_3 . From geometry, the conversion of Mn_3O_4 , α , is

Equation 10
$$\alpha = 1 - a^3 / b^3.$$

Integrating Equation 9 and substituting in the above expression yields the Ginstling-Brounshtein equation,

Equation 11
$$1 - \left(\frac{2}{3}\right)\alpha - (1 - \alpha)^{2/3} = 2DC_0 V_m t / b^2.$$

The above equation is represented by

Equation 12
$$f(\alpha) = kt$$

with the kinetic rate constant, k , given by

Equation 13
$$k = 2DC_0 V_m / b^2.$$

A plot of the left side of Equation 11 versus time should yield a straight line with slope k . Figure 5 shows that the initial part of the reaction follows the Ginstling-Brounshtein model up to 60% conversion of Na_2CO_3 . It is presumed that the deviation from the model at higher conversions is due to discontinuities developing in the Na_2CO_3

layer. The Ginstling-Brounshtein model was used to determine kinetic rate constants under different reaction conditions.

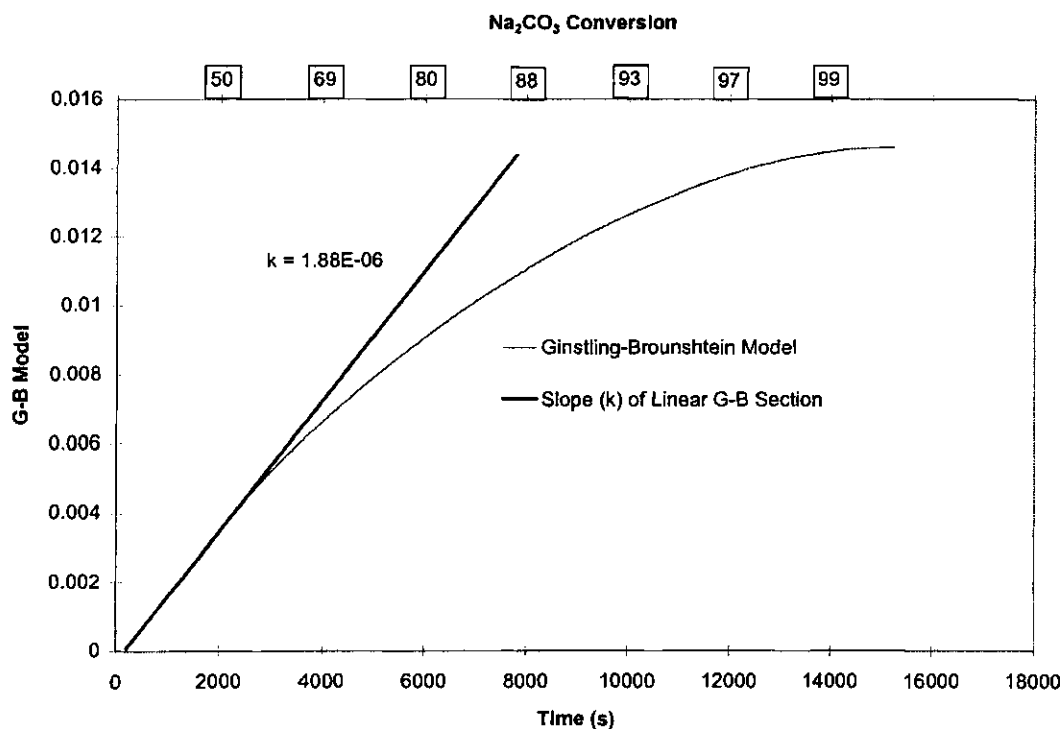


Figure 5. G-B function versus time. 827°C, 23 μm Mn_3O_4 , $\text{Mn}_3\text{O}_4\text{:Na}_2\text{CO}_3 = 3\text{:}1$.

Effect of Temperature

An important parameter in chemical reaction rates is the temperature. Solid-solid reactions are usually limited in rate by the movement of the diffusing species through the product layer, which limits the overall reaction rate. With an increase in temperature, the diffusivity increases, leading to higher overall rates of reaction.

Additionally, increases in temperature can lead to phase changes such as melting and vaporization. For the Mn_3O_4 and Na_2CO_3 -based direct causticizing system, the melting point of Na_2CO_3 is an issue. It occurs at 850°C and is depressed by the presence

of Na_2S . The melting of Na_2CO_3 will change the reaction system from solid-solid with gas evolution to solid-liquid with gas evolution. However, the reaction mechanism is likely to stay the same. The major difference is that the Na_2CO_3 will diffuse through the product layer as a liquid rather than a solid. The barrier to diffusion, the product layer, will still remain. The G-B model is also valid for a diffusing species that is liquid. In fact, it is more likely to quickly satisfy the assumption of complete surface coverage of the reactant particle.

Temperature effects in chemical reactions are commonly described by the Arrhenius equation.

Equation 14
$$k = Ae^{(-E/RT)}$$

A plot of $\ln k$ versus $1/T$ usually yields a straight line whose slope has the units of inverse temperature. When the slope is multiplied by R , the universal gas constant, an activation energy, E , is obtained. The intercept yields the frequency factor, A .

Experiments were conducted to investigate the kinetics of the reaction between Mn_3O_4 and Na_2CO_3 as both a solid and a melt. In the solid state, $23\mu\text{m}$ Mn_3O_4 was used with $\text{Mn}_3\text{O}_4:\text{Na}_2\text{CO}_3$ initial molar ratios of 1:4 and 1:1. The temperature range of 650 to 850°C was investigated. With Na_2CO_3 in the molten state, the $227\mu\text{m}$ Mn_3O_4 was used with $\text{Mn}_3\text{O}_4:\text{Na}_2\text{CO}_3$ initial ratios of 1:1. The temperature range was 870 to 950°C .

Figure 6 shows the Arrhenius plots for the reactions in the solid state. The slopes of $-25,251 \pm 1047$ and $-24,468 \pm 3295 \text{ }^\circ\text{K}^{-1}$ yield activation energies, E , of 210 ± 9 and $203 \pm 27 \text{ kJ/mol}$ respectively. The intercepts of 14.016 ± 1.021 and 11.376 ± 3.213 yield frequency factors, A , of 1.2×10^6 and $8.7 \times 10^4 \text{ s}^{-1}$ respectively. The difference in activation energies is within experimental error. However, the frequency factors are different as a

result of different initial molar ratios of reactants. This suggests that the frequency factor, A , for the diffusivity is a function of the initial molar ratio of reactants. This relationship will be investigated below.

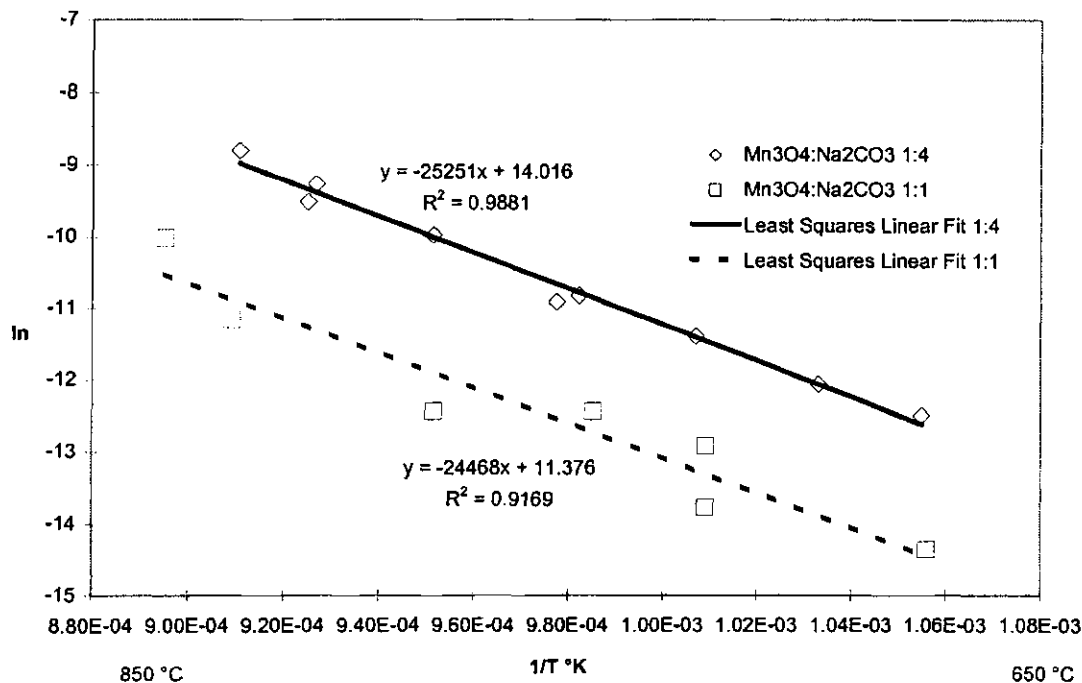


Figure 6. Arrhenius plot for solid-solid reaction. Temperature range 650-850°C. $Mn_3O_4:Na_2CO_3$ initial molar ratios of 1:4 and 1:1. $23\mu m$ Mn_3O_4 .

The Arrhenius plot for the molten experiments is shown in Figure 7. From the slope of $-20,872 \pm 980$, an activation energy of 174 ± 8 kJ/mol is obtained. This indicates that the barrier to diffusion has a smaller temperature dependence when the Na_2CO_3 is molten. However, a large increase in the kinetic rate constant occurs upon melting. The kinetic rate constant at 850°C, extrapolated from the solid-solid data for a $Mn_3O_4:Na_2CO_3$ ratio of 1:1 and $227\mu m$ Mn_3O_4 particles, is 6.34×10^{-6} . The reaction rate constant at the

same temperature, extrapolated from the molten data, is 2.58×10^{-4} . The transition from solid to molten Na_2CO_3 increases the reaction rate constant by 40 times at 850°C .

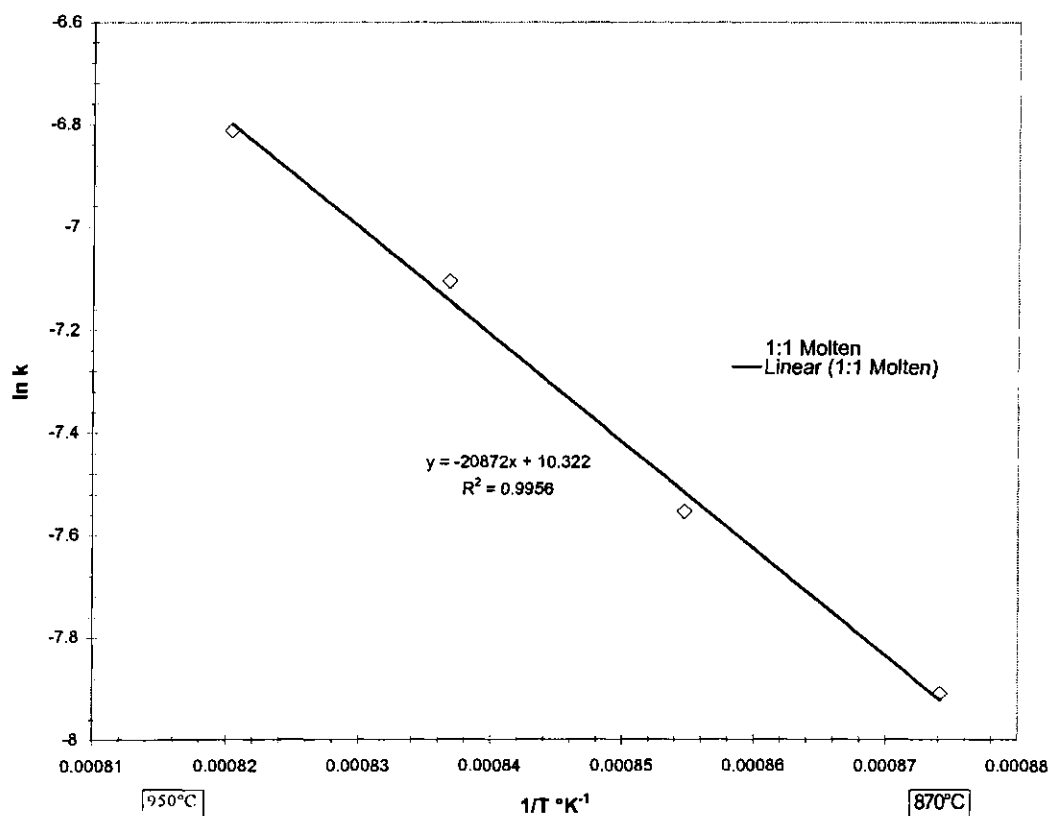


Figure 7. Arrhenius plot for solid-liquid reaction. Temperature range 870 – 950°C . Mn_3O_4 : Na_2CO_3 initial molar ratio of 1:1. $227\mu\text{m}$ Mn_3O_4 .

The values for the activation energies compare to findings of other authors for different systems. Zou reported an activation energy of 216 kJ/mol for the Na_2CO_3 and TiO_2 system[12]. Johnson and Gallagher[13] found that the Li_2CO_3 and Fe_2O_3 system obeyed the Ginstling-Brounshtein equation. A value of 210 kJ/mol for the activation energy was found over the temperature range 380 to 510°C . They suggested that the

Li_2CO_3 migrated to cover the Fe_2O_3 particles and reacted to release CO_2 ; the rate limiting process was the diffusion of Li^+ across the LiFeO_2 product layer.

Effect of Particle Size

Increasing the particle size of the Mn_3O_4 was hypothesized to reduce the reaction rate for the direct causticizing reaction. A larger particle results in a longer diffusion path for the diffusing species, in order to reach complete conversion of the particle. The longer diffusion path decreases the rate at which the diffusing species can reach the reaction interface, slowing the reaction.

The Ginstling-Brounshtein model was derived for spherical reactants. In the model, the reaction rate constant, k , is proportional to $1/r^2$ as shown in Equation 13. The proportionality is equivalent to $2DC_oV_m$. If the constants 2, C_o , and V_m are combined with the diffusivity frequency factor, the following equations result.

$$\text{Equation 15} \quad k = \frac{A_o e^{-E/RT}}{r^2}$$

$$\text{Equation 16} \quad A_o = 2C_oV_m A$$

Taking the natural logarithm of Equation 15 and letting $A_o e^{-E/RT}$ equal B yields the following.

$$\text{Equation 17} \quad \ln k = \ln B - 2 \ln r$$

A plot of $\ln k$ versus $\ln r$ should yield a straight line with slope -2 . The exponential of the intercept should yield the proportionality, B . Figure 8 is a plot of $\ln k$ versus $\ln r$ for three different initial molar ratios of reactants.

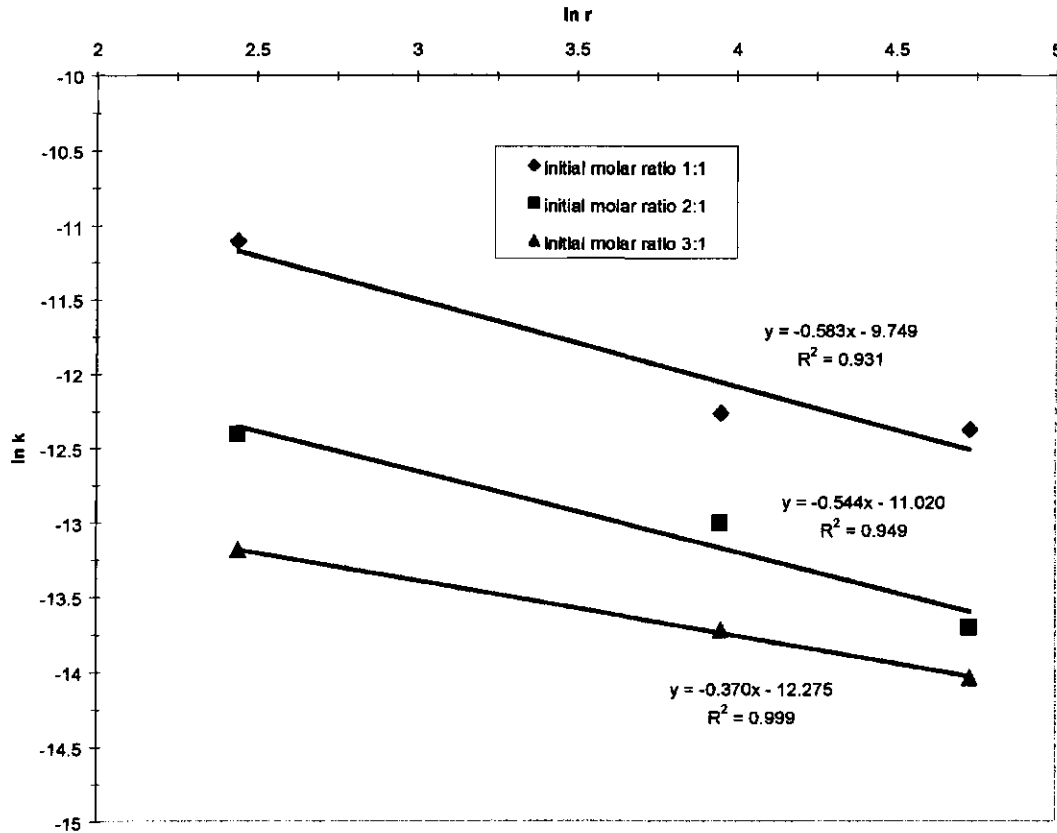


Figure 8. The effect of volume mean particle size on reaction rate. 23, 104, and 227 μm Mn_3O_4 .

Slopes of -0.583 ± 0.158 , -0.544 ± 0.126 , and -0.370 ± 0.012 were found for initial molar ratios of 1, 2, and 3 respectively. The average of these slopes is approximately -0.5 . This indicates that the particle size dependence is not $1/r^2$ but instead $1/r^{0.5}$.

A strong conclusion on the effect of the particle size on reaction rate cannot be inferred from these results. The deviation from the theoretical $1/r^2$ dependence is not entirely surprising. SEM images of the starting materials show that the particles are very rough approximations for spheres. In addition, the 23 μm Mn_3O_4 was mechanically treated with the mortar and pestle to produce particles with different characteristics than the 104 μm and 227 μm fractions. Because of

the deviation from the model assumptions, only a qualitative conclusion can be made. An increase in Mn_3O_4 particle size results in a decrease in the reaction rate constant.

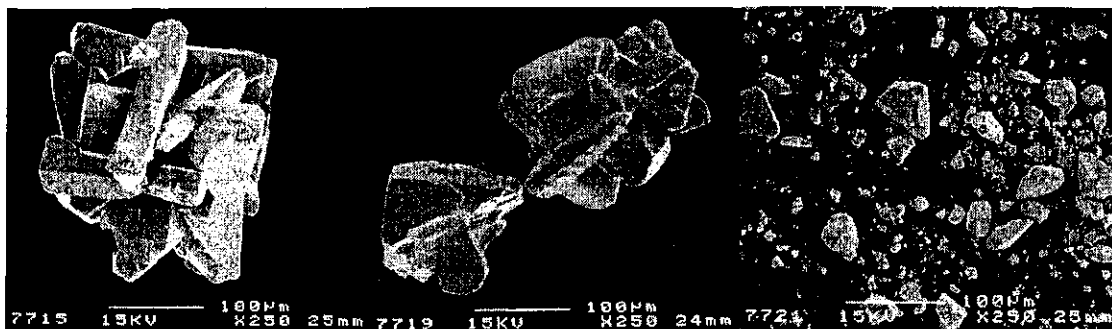


Figure 9. SEM images of Mn_3O_4 prior to reaction. 227, 104, and $23\mu\text{m}$ volume mean equivalent diameters. 250x magnification.

Effect of Initial Molar Ratio of Reactants

The overall goal of direct causticizing is to convert Na_2CO_3 to NaOH . High conversions of Na_2CO_3 are desired. Because of the 1:1 stoichiometry of the reaction, areas of practical interest to study include stoichiometric amounts of reactants, or an excess of Mn_3O_4 . With an excess of Na_2CO_3 , complete conversion of the component would not occur.

A series of experiments were conducted to investigate the effects of stoichiometric excesses of Mn_3O_4 in the reaction mixture. The results are presented in Figure 10 for 23, 104, and $227\mu\text{m}$ particles at 827°C and also for $23\mu\text{m}$ Mn_3O_4 particles at 740°C . In these experiments, the Na_2CO_3 was the limiting reactant, being entirely consumed. When excess Na_2CO_3 was initially present in the reaction mixture, the kinetic rate constant was higher. This relationship was well described by an empirically fit power law.

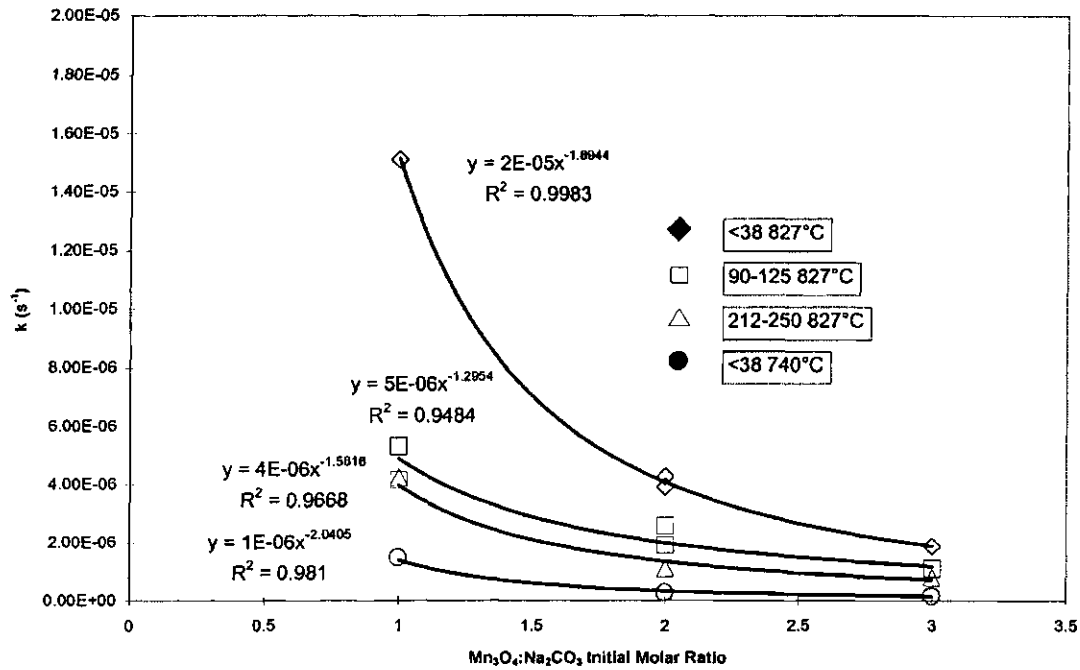


Figure 10. The kinetic rate constant versus the initial molar ratio of reactants. 740 and 827°C. Various Mn_3O_4 particle sizes.

The change in the reaction rate constant with different initial molar ratios of reactants suggests that the diffusivity frequency factor has a power law dependence on the initial molar ratio.

Equation 18

$$A = \phi \left(\frac{Mn_3O_4}{Na_2CO_3} \right)^\varepsilon$$

The power ε , and prepower factor ϕ , are dependent on the particles used in the reactions. Different particle sizes, pretreatments, and morphologies appear to change their values.

By combining the experimental results with Equations 15, 16, and 18, the Ginstling-Brounshtein kinetic rate constant for the reaction between Mn_3O_4 and Na_2CO_3 can be summarized with the following expression.

Equation 19

$$k = \frac{2\phi \left(\frac{Mn_3O_4}{Na_2CO_3} \right)^\epsilon e^{-E/RT} C_o V_m}{r^{0.5}}$$

E is 206 kJ/mol between 650 and 850°C and 174 kJ/mol between 850 and 950°C. ϕ and ϵ are functions of the specific reactants used.

Process Efficiency

A mass balance on the total sodium into the process, as Na_2CO_3 , and the amount of sodium recovered in the post hydrolysis filtrate, as Na_2CO_3 and $NaOH$, was constructed. It was termed the Total Sodium Recovery and defined as follows.

Equation 20

$$\text{Total Sodium Recovery (\%)} = \frac{\text{mol Na recovered in filtrate}}{\text{mol Na into direct causticizing reaction as } Na_2CO_3} \times 100$$

The efficiency of the direct causticizing reaction was represented by the Na_2CO_3 conversion determined from the total CO_2 evolution. This conversion was based on the CO_2 release as a function of the total Na_2CO_3 used in the reaction. The direct causticizing efficiency is simply

Equation 21

$$Eff_{dc} = \alpha_{Na_2CO_3} = CO_{2t} / Na_2CO_{3i} \times 100$$

where CO_{2t} is the total moles of CO_2 evolved and Na_2CO_{3i} is the initial number of moles of Na_2CO_3 .

The aqueous filtrate from the hydrolysis step contained NaOH and Na₂CO₃. The overall efficiency was defined in a manner similar to that used for CaO-based recovery cycles.

Equation 22
$$Eff_o = \frac{\text{mol NaOH}}{\text{mol NaOH} + 2 \times \text{mol Na}_2\text{CO}_3} \times 100$$

The moles of NaOH and Na₂CO₃ are determined in an aliquot of the filtrate to calculate the overall efficiency. The overall efficiency, similar to causticity, is an indication of the quality of the pulping liquor leaving the chemical recovery stage.

The direct causticizing reaction and the hydrolysis step do not appear to be equilibrium-limited. Values for the various efficiencies are presented in Table 1.

<i>Temp (°C)</i>	<i>Initial Molar Ratio</i>	<i>Mn₃O₄ Particle Size (μm)</i>	<i>Total Sodium Recovery (%)</i>	<i>Eff_{DC} (%)</i>	<i>Eff_o (%)</i>
830	1:1	104	100.2	91.2	86.9
830	2:1	104	100.7	99.2	100.0
830	3:1	104	99.8	99.8	94.6
871	1:1	227	102.6	98.7	94.0
897	1:1	227	99.7	98.1	93.3
922	1:1	227	98.1	100.2	100.0
946	1:1	227	98.8	99.0	100.0

Table 1. Process efficiencies and material balance results for the overall direct causticizing process.

In the examples in Table 1, the direct causticizing reactions were run essentially to completion. The only exception was the 830°C, 1:1 reaction. It was stopped prior to completion of the reaction, so complete conversion was not obtained.

Effect of Sodium Sulfide

Na₂S was added to the Na₂CO₃ and Mn₃O₄ reaction mixture with a sulfide initial molar ratio, Na₂S:Na₂CO₃, of 0.33:1. This sulfide addition depressed the melting point of

the mixture below 800°C. In order to conduct the reaction in the solid state, a temperature of 740°C was chosen to study the effects of Na₂S.

Following the reaction, the material was transferred to a nitrogen-filled container, then immediately analyzed with XRD. The experiment was repeated with the product being immediately transferred to the hydrolysis step instead of the XRD. The hydrolysis was conducted with a nitrogen purge. Following hydrolysis, some filtrate was removed for analysis directly from the solution to avoid air contact during the filtering operation. The filtrate was analyzed with the ABC titration and capillary ion electrophoresis.

The XRD analysis of the pre hydrolysis solid material indicated that some NaMnO₂ was formed. Mn₃O₄ was also present. In addition, there was also a strong peak for MnO. There were no peaks for Na₂S or MnS.

Analysis of the filtrate from hydrolysis with the ABC titration also did not detect any Na₂S. Analysis of the filtrate with capillary ion electrophoresis indicated the sulfur species were transformed into sulfate and thiosulfate.

Thermodynamic calculation of the Gibbs Free Energy of Reaction suggests that Mn₃O₄ can oxidize Na₂S to Na₂SO₄ over all temperature ranges of interest, as seen in Table 2.

Temp (°C)	Na ₂ S + 4Mn ₃ O ₄ ⇌ Na ₂ SO ₄ + 12MnO G _r (kJ/mol)
100	-159.0
400	-197.8
700	-245.0
1000	-306.4

Table 2. Gibbs Free Energy of Reaction.

With the Mn₃O₄-based direct causticizing system, the reaction between

Na_2S and Mn_3O_4 remains a problem. Because the goal of direct causticizing is to convert Na_2CO_3 into NaOH , a high efficiency for that step would be required. Looking at the worst case, if the $\text{Na}_2\text{S}:\text{Na}_2\text{CO}_3$ ratio were 0.33:1, the $\text{Mn}_3\text{O}_4:\text{Na}_2\text{CO}_3$ ratio would need to be 2.3:1 to ensure complete conversion of Na_2CO_3 to NaMnO_2 . 1 mole would be used for the reaction with Na_2CO_3 , and 1.3 moles would react with the Na_2S . This would still result in an unfavorable situation because the Na_2S would be converted to Na_2SO_4 . An additional process step or method would be needed to reduce the Na_2SO_4 . Similarly, the MnO would need to undergo an oxidation step to form Mn_3O_4 .

CONCLUSIONS

The overall purpose of this work was to investigate the feasibility of developing a manganese-oxide based direct causticizing process for the recovery of kraft black liquors. The direct causticizing reaction between Mn_3O_4 and Na_2CO_3 was determined to occur with a 1:1 stoichiometry.

The temperature, particle size, and initial molar ratio of reactants were studied to see how they affected the reaction kinetics for the direct causticizing reaction between Mn_3O_4 and Na_2CO_3 . In the solid state, from 650 to 850°C, the reaction had an activation energy of 206 kJ/mol. With molten Na_2CO_3 , in the temperature range of 850 to 950°C, the reaction had an activation energy of 174 kJ/mol. Transition from the solid-solid reaction to the solid-liquid reaction increased the reaction rate constant by a factor of 40.

The overall particle radius of the Mn_3O_4 was found to have an effect on the reaction rate constants. Increases in the particle size slowed the reaction. However, the reaction rate did not follow the $1/r^2$ dependence on particle size as expected. This deviation is attributed to the nonspherical nature of the Mn_3O_4 particles used in this study.

An increase in the initial molar ratio of $\text{Mn}_3\text{O}_4:\text{Na}_2\text{CO}_3$ increased the rate of Na_2CO_3 conversion. This corresponded to a decrease in the reaction rate constant based on the conversion of Mn_3O_4 . The effect of the initial molar ratio of reactants on the reaction rate constant followed an empirical power law dependence.

The reaction between Mn_3O_4 and Na_2CO_3 in the temperature range of 650 to 950°C is well described by the Ginstling-Brounshtein product-layer diffusion controlled model.

The direct causticizing reaction and subsequent hydrolysis of the product had very high efficiencies. Neither step was found to be equilibrium-limited. In addition, the Mn_3O_4 could be regenerated in the lab with no loss of material.

The presence of Na_2S was found to have a negative impact on the direct causticizing reaction. Na_2S reduced Mn_3O_4 to MnO while being oxidized to Na_2SO_4 . For direct causticizing of kraft smelt with Mn_3O_4 to be feasible, the deactivated MnO would need to undergo a reoxidation step. In addition, reduction of Na_2SO_4 would be required to regenerate Na_2S .

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