This article was downloaded by: [142.58.101.27] On: 11 October 2013, At: 10:18 Publisher: Taylor & Francis Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of the Air & Waste Management Association Publication details, including instructions for authors and subscription information: http://www.tandfonline.com/loi/uawm20

Preparation of Calcium Silicate Absorbent from Iron Blast Furnace Slag

Lia F. Brodnax ^a & Gary T. Rochelle ^b

^a Bay Area Air Quality Management District, San Francisco, California, USA

^b Department of Chemical Engineering , University of Texas at Austin , Texas , USA Published online: 27 Dec 2011.

To cite this article: Lia F. Brodnax & Gary T. Rochelle (2000) Preparation of Calcium Silicate Absorbent from Iron Blast Furnace Slag, Journal of the Air & Waste Management Association, 50:9, 1655-1662, DOI: 10.1080/10473289.2000.10464191

To link to this article: <u>http://dx.doi.org/10.1080/10473289.2000.10464191</u>

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at http://www.tandfonline.com/page/terms-and-conditions

Preparation of Calcium Silicate Absorbent from Iron Blast Furnace Slag

Lia F. Brodnax

Bay Area Air Quality Management District, San Francisco, California

Gary T. Rochelle

Department of Chemical Engineering, University of Texas at Austin, Texas

ABSTRACT

Calcium silicate hydrate (CSH) solids were prepared from hydrated lime and iron blast furnace slag in an aqueous agitated slurry at 92 °C. While it was hoped a minimal lime/slag ratio could be used to create near-amorphous CSH, the surface area of the product improved by increasing the lime/slag weight ratio to 2. The addition of gypsum to the lime/slag system dramatically improved the formation of surface area, creating solids with 139 m²/g after 30 hr of reaction when only a minimal amount of lime was present. The SO₂ reactivity of solids prepared with gypsum greatly exceeded that of hydrated lime, achieving greater than 70-80% conversion of the alkalinity after 1 hr of reaction with SO₂. The use of CaCl₂ as an additive to the lime/slag system, in lieu of gypsum, also produced high-surface-area solids, 115 m²/g after 21 hr of reaction. However, the SO₂ reactivity of these sorbents was relatively low given the high surface area. This emphasized that the correlation between surface area and SO₂ reactivity was highly dependent on the solid phase, which was subsequently dependent on slurry composition.

IMPLICATIONS

Calcium silicate solids prepared from iron blast furnace slag were substantially more reactive with SO₂ than hydrated lime, the typical industrial sorbent used in dry desulfurization processes. Sorbent with 122 m²/g and an alkalinity equivalent to 0.63 g Ca(OH)₂ was prepared under agitated conditions at 92 °C from a 0.5/1/0.1 lime/ slag/gypsum (wt) mixture. While the total alkalinity per mass was lower, SO₂ at 58% relative humidity (RH) was able to react 79% of the alkalinity of these solids compared with an average conversion of 30% for hydrated lime. It is believed that solids prepared from 0.1/1/0.1 lime/ slag/gypsum, with a surface area of 139 m²/g, would exhibit similar SO₂ reactivity. This presents the optimum case, preparing highly reactive solids using a minimal quantity of additional lime and gypsum.

INTRODUCTION

The use of an alkaline solid to remove SO_2 from a gas stream is one of several options for tail-end SO_2 control from a variety of smaller sources. Typically, hydrated lime has been used as the industrial sorbent for dry or semidry SO_2 scrubbing. Unfortunately, the precipitated calcium sulfite product tends to coat the lime surface, leading to significantly slower rates of reaction. The result is low conversion of the lime and, therefore, an increased cost of buying and disposing of largely unreacted reagent.

Calcium silicate hydrates (CSHs) have been shown to be highly effective reagents in dry scrubbing systems. The silicates have a higher surface area than lime and are able to attain higher conversions of the alkalinity present in the solids.^{1,2} Previous calcium silicate sorbent research has focused on the preparation of solids from lime and fly ash, though it has been shown that glass, silica fume, and other amorphous silicas can be used in lieu of fly ash.³⁻⁷

The formation of silicates from lime and an amorphous SiO_2 source in an aqueous environment below 100 °C is described in reactions 1–3. The dissolution of the lime releases Ca^{2+} and OH^- into solution. The increased solution pH facilitates the dissolution of the amorphous $(SiO_2)_x$ shown in reaction 2. Dissolved $Si(OH)_5^-$ and Ca^{2+} then precipitate to form high-surface-area, nearly amorphous CSH. Above 100 °C, the precipitated CSH is believed to be comprised of less amorphous, more crystalline tobermorite phases.⁸

$$Ca(OH)_2 \leftrightarrow Ca^{2+} + 2OH^-$$
 (1)

$$(\text{SiO}_2)_{X} + 2\text{H}_2\text{O} + \text{OH}^- \leftrightarrow (\text{SiO}_2)_{X-1} + \text{Si}(\text{OH})_5^-$$
 (2)

$$Ca^{2+} + ySi(OH)_{5}^{-} + (2 - y)OH^{-} + (z - 2y - 1)H_{2}O \rightarrow$$

$$(CaO)(SiO_{2})_{y}(H_{2}O)_{z}(CSH)$$
(3)

This research investigated the formation of calcium silicates using iron blast furnace slag as the amorphous SiO₂ source. Slag is the secondary product of an iron blast furnace, consisting of lime flux and the SiO_2 , sulfur, and other impurities separated by the flux from the iron ore. Slag was chosen for study due to the large intrinsic Ca concentration, shown in Table 1, roughly equal parts Ca to Si. This presents an interesting possibility: the activation of slag as an alkaline sorbent for desulfurization applications with a minimal amount of additional lime, thereby reducing the need to acquire (and ship) raw material. Benchscale experiments conducted with slag focused on the effects of the lime/slag/additive recipe on the aqueous slurry chemistry and, therefore, the final product solids.

EXPERIMENTAL

This section describes the experimental apparatus and procedures used to prepare calcium silicates from lime and blast furnace slag. The apparatus utilized to measure the gas/solid reaction between the sorbents and SO_2 is also described. A more detailed description of the experimental procedures is published elsewhere.^{6,7}

Sorbent Preparation

The ground granulated iron blast furnace slag used in this work was a sample donated by Koch Industries, Inc., with a measured Brunauer-Emmett-Teller (BET) surface area of 3.62 m²/g. The lime was a rotary mill hydrate (Code MR200) donated by the Mississippi Lime Co. with a measured BET surface area of 21.6 m²/g. The gypsum (CaSO₄•2H₂O) and CaCl₂ additives were reagent grade material.

Agitated Solids Preparation. Sorbents were prepared at 92 °C from agitated batch slurries in a 500-mL jacketed Pyrex reactor connected to an ethylene glycol temperature-control bath. As expected, the Pyrex reactor also reacted with the slurry as an amorphous SiO_2 source. However, this effect was minimized by the large relative surface area of the ground slag sample compared with the reactor walls. The slurry was stirred at 350 rpm with a mechanical agitator placed through a plexiglass lid on the reactor. Though the reactor was covered to minimize water loss, it was not airtight. Several samples were withdrawn via syringe at various reaction times. The samples were filtered through a medium filter paper, and the solids were vacuum-dried

Table 1. Comparison of a typical fly ash with iron blast furnace slag.^{9,10}

at 90 °C. The liquid filtrate was filtered again through a 0.45- μ m filter and stored in polypropylene bottles for later analysis.

Nonagitated Solids Preparation. Solids were prepared without agitation in single glass sample vials (~8 mL). The unreacted solids and water were mixed and weighed in the vial, which was then capped. Sets of vials were placed in a Blue M convection oven that controlled the temperature at 92 °C, and individual samples were removed at the appropriate reaction time. They were weighed for water loss (<5%) and vacuum-dried at 90 °C for 6–24 hr. Since the samples were not filtered prior to drying, any dissolved species in the slurry solution must have precipitated on the solid surfaces. As expected, the glass vials also reacted with the slurry as an amorphous SiO₂ source. However, this effect was minimized by the large relative surface area of the ground slag sample compared with the vial walls.

Sorbent Preparation Sample Analysis. All the solid samples were analyzed for BET surface area by nitrogen adsorption. Nitrogen adsorption was also used to determine the porosity of a few samples. Selected samples were also characterized using scanning electron microscopy (SEM) and X-ray diffraction. The "divalent alkalinity" (molar equivalent to Ca2+) was measured by dissolving the solids in 0.1 M HCl and back-titrating with 0.2 M NaOH to the phenolphthalein end point. Liquid filtrate samples were analyzed for pH at ambient temperature and for Ca²⁺, K⁺, and Na⁺ by atomic absorption (AA) spectrophotometry. Aqueous sulfide was measured by titrating with AgNO, to the potentiometric end point as measured with a silver sulfide electrode. The composition of the solid product was measured by "selective dissolution," in which the solids were dissolved in 0.1 M HCl and the resulting liquid analyzed for Ca2+, Si, and Na+ by AA.

SO, Reactivity

The reaction between solid sorbents and SO_2 was measured using a packed fixed-bed glass reactor. The sorbent (0.1 g) was mixed with an inert SiO_2 sand (30 g) for good dispersion across the bed, and the mixture was suspended on a glass frit within the reactor. The reactor was immersed in a water bath for temperature control at 50 °C.

Composition (wt %) S SiO, Al₂O₃ CaO Mg0 Na_gO K,O Fe₂O₃ Ti0 Fly Ash 51.6 24.7 5.2 1.8 0.5 3.3 7.8 1.4 Slag 30-45 5 - 1430-45 8-15 0-1 0 - 10-0.75 0.1.5 0-3.5 A synthesized flue gas was created by diluting compressed SO_2/N_2 with N_2 utilizing mass flow controllers. The gas stream was humidified to 58% relative humidity (RH) using a syringe pump and furnace. The synthesized flue gas flowed downward through the packed bed reactor where the sorbent reacted with and removed the SO_2 . The outlet was diluted (~20×) with house air to prevent downstream condensation, and the SO_2 concentration was measured and recorded using a Thermo Electron Pulsed Fluorescent Analyzer (Series 43).

RESULTS

This work investigated the formation of calcium silicate solids from the reaction between iron blast furnace slag and lime. Since SO_2 reactivity for calcium silicate sorbents from fly ash was correlated with the amount of moisture the solids can hold within the pore structure,¹¹ and this moisture was shown to correlate with surface area,¹² surface area was used as the convenient initial measurement of the reactivity of the product solids. This simplification should hold true only as long as the solid composition and phase remains constant. For the most promising solids, that is, those with the highest surface area, SO_2 reactivity was measured directly.

Sulfide Control

One of the more unique components in slag, as compared with fly ash or container glass, is sulfide. The nominal concentration of sulfide was expected to be 0–3.5 wt % (Table 1) of the slag. Gaseous H_2S is a nuisance at 0.13 ppm, an irritant at 20 ppm, and a dangerous gas at 150 ppm.¹³ Therefore, it was decided that finding a suitable method of controlling the sulfide release during sorbent preparation would be useful for both bench-scale and industrial applications.

Solution sulfide was measured by potentiometric titration. Figure 1 shows the effects of several different additives on the measured sulfide concentration. Na₂S₂O₃ and Na₂SO₃ were added, at a level of 0.1 M each at the start of the experiment, with the expectation that the sulfide might convert to elemental sulfur or thiosulfate. It is clear from Figure 1, however, that the SO₃^{2–}/S₂O₃^{2–} mixture, in fact, increased the measured sulfide. Furthermore, the presence of these additives decreased the surface area of the product solids.

Figure 1 also shows the results of the addition of FeSO_4 at an initial level of 0.13 M. It was hypothesized that the Fe²⁺ would precipitate the sulfide as FeS. While it was clear that Fe²⁺ reduced the amount of sulfide in solution, it appeared that there was a measurable equilibrium limitation to the sulfide concentration.

 $\rm H_2O_2$ was added to the system in an attempt to oxidize the sulfide directly into $\rm SO_4^{\ 2-}$ as it was released from



Figure 1. Effect of additives on sulfide concentration. 92 °C; agitated; 400-mL water; 75-g lime; 25-g slag. H_2O_2 addition: intermittent addition as shown on graph. Fe²⁺: 0.13M FeSO₄•7H₂O added at start. SO₃²⁻/S₂O₃²⁻: 0.1M Na₂SO₃/0.1M Na₂S₂O₃ added at start.

the slag. The H_2O_2 was added intermittently, as shown in Figure 1. The addition of H_2O_2 eliminated sulfide below detection by either the electrode method or by lead acetate paper, which has a detection limit of 25 ppm. The addition of Fe²⁺ or H_2O_2 did not significantly affect the rate of surface area formation.

It was decided to utilize the procedure of H_2O_2 addition for the bulk of experiments with slag. The reaction slurry was tested periodically (every 1–2 hr) by lead acetate paper. If a positive reading was obtained, H_2O_2 was added in 3- to 5-mL increments until the lead acetate tested negative. While H_2O_2 might be considered a relatively expensive additive in industrial settings, the amounts used could easily be minimized, and the benefits of preventing sulfide release would have to be weighed.

Effect of Lime/Slag Ratio

As mentioned previously, an interesting concept regarding SiO₂ sources with extremely high intrinsic alkalinity is the possibility of creating a reactive alkaline sorbent with a minimum of lime. An initial OH⁻ level would be required to initiate the breakdown of the SiO₂ matrix as shown in eq 2. This initial OH⁻ concentration may come from added lime, NaOH, or perhaps from the dissolution of alkali from the SiO₂ itself, thereby creating a self-catalyzing effect. Once the SiO₂ matrix starts to dissolve, the intrinsic Ca²⁺, which is simultaneously dissolving, should fuel the formation of calcium silicates according to eq 3.

Peterson¹⁴ and Peterson and Rochelle¹⁵ showed that high-calcium fly ash could be activated for reaction without the addition of lime. The addition of NaOH, however, increased the initial dissolution of fly ash, and thereby increased the SO₂ reactivity. A tradeoff was observed between the increased dissolution rates of the SiO₂ and the suppression of the Ca²⁺ concentration by reaction 1 caused by high OH⁻ concentration. Stroud¹² also showed that a small amount of hydrated lime (0.1 g Ca(OH)₂/g fly ash) would activate high-calcium fly ash.

The effect of the lime/slag ratio on surface area formation was investigated in this research to determine if sorbent could be prepared with a minimum amount of additional lime. Figure 2 shows that slag alone (0/1 lime/ slag) increased in surface area from 3.6 to 25 m²/g within the first 4 hr, but remained constant thereafter. The addition of lime to the system increased the rate of surface-area formation over reaction times up to 50 hr. It appeared, within the experimental scatter and the ratios tested, that the absolute surface area increased with lime addition up to a lime/slag wt ratio of 2/1. At higher ratios, the surface area of the product decreased, indicating that the excess hydrated lime reduced the average surface area of the solids.

While it was hoped that a minimal amount of lime would be sufficient, it is clear that a larger lime concentration enhanced the rate of surface area formation. Near-amorphous CSH is defined by a Ca/SiO_2 molar ratio of 0.8–2.0.⁸ For the low lime limit of a Ca/Si ratio of 0.8, and 45 wt % of Ca in the slag, it is conceivable to form CSH without an additional Ca source. One hypothesis to explain the larger lime requirement is that at low lime loading, the system becomes lime dissolution limited. The pH and Ca concentration in the bulk solution drop, and the product precipitates on the surface of the lime rather than on the surface of the slag. Therefore, the remaining undissolved lime is essentially coated, causing a further reduction in lime dissolution, and the reaction shown in eq 2 slows to a very low rate.

While the surface area data shown in Figure 2 presented a fairly clear trend, the Ca concentration measurements



Figure 2. Effect of lime/slag ratio on surface area formation. 92 °C; agitated and nonagitated; 13–50-wt % solids. Labels indicate lime/ slag wt ratio; no additives.

exhibited considerable experimental scatter. The scatter may have resulted from filtrate containing small particles of lime or other Ca-containing solids. However, identical procedures in the preparation of glass/lime sorbents⁷ did not produce the same level of scatter. In spite of the scatter, the average Ca concentration increased from 5.3 mM (5 observations/ σ = 2.06) to 11.1 mM (8 observations/ σ = 3.35) when the lime/slag ratio increased from 0.5 to 3, supporting the hypothesis that the system was lime dissolution limited at low lime/slag ratios.

Arthur and Rochelle⁶ showed that agitation had a positive effect on the lime/glass/gypsum only after a fairly high surface area was formed. Figure 3 shows that within the experimental scatter, agitation would not affect the lime/slag system for reaction times less than 50 hr. The apparent increase in surface area with an increasing lime/slag ratio from 2 to 3 is indicative of the normalized surface area axis, which increases with relative decreases in slag loading. The normalized axis was used in Figure 3 to spread the data and facilitate the observation of the experimental scatter.

Effect of Additives on Sorbent Formation

This section presents results from experiments in which gypsum or $CaCl_2$ was added to the lime/slag system. All experiments discussed in this section were conducted at 92 °C with agitation, so that slurry solution analysis would be possible. The sulfide was controlled by the addition of H_2O_2 as mentioned previously.

Effect of Gypsum. While hydrated lime and SiO_2 are the primary reactants of interest, it has been shown that adding other compounds to the reaction slurry, such as gypsum or CaCl₂, produced sorbents from fly ash or glass with increased surface area and reactivity.^{3,6,7,16,17} The additives were added to counter the "calcium effect" seen in both fly ash and glass systems.



Figure 3. Effect of agitation on surface area formation. 92 °C; 20-wt % solids. Labels indicate lime/slag wt ratio.

The calcium effect was reported by Peterson¹⁴ and Kind³ as a result of either the addition of NaOH to the slurry or KOH dissolution from the fly ash. NaOH or KOH in solution share OH⁻ as a common ion with lime. As eq 1 shows, if the OH⁻ concentration becomes too large, the concentration of Ca2+ in solution will be depressed. Kind3 showed gypsum and CaCl, to be effective additives to counter this common ion effect.

It was shown that the presence of a gypsum solid phase produced an increased Ca2+ concentration over the duration of the experiment by providing a common SO₄²⁻ ion for Na⁺ and K⁺ released from the glass or fly ash to associate with, as seen in eqs 4 and 5. It is believed that this allowed for a higher reaction rate, producing solids with much higher surface area than systems without gypsum.

$$CaSO_4 + 2KOH \leftrightarrow K_2SO_4 + Ca(OH)_2$$
(4)

$$CaSO_4 + 2NaOH \leftrightarrow Na_2SO_4 + Ca(OH)_2$$
 (5)

Figure 4 shows that the presence of gypsum increased surface area formation dramatically for lime/slag ratios of 0.5 and 1. In fact, the addition of a small amount of gypsum to the system at 0.5/1 lime/slag increased the surface area by almost 3-fold.

Figure 5 shows the Ca²⁺ concentration in solution from experiments with and without gypsum. For the fly ash and glass systems, it was shown that without gypsum present, the Ca2+ concentration would fall to ~1 mM.3,7 For the slag system shown in Figure 5, the experiments without gypsum sustained a Ca2+ concentration of ~5 mM. In light of experience with fly ash and glass, this concentration was expected to be sufficient to maintain a reasonable rate of surface area formation. However, it is evident in Figure 4 that the reaction was relatively slow. While there was substantial scatter in the Ca²⁺ data, the

0.5/1 - no additives

1/1 - no additives

0.1/1/0.1 - gypsum 0.5/1/0.1 - gypsum

1/1/0.1 - gypsum 0.5/1/0.03 (50mM) CaCl

0.5/1/0.06 (90mM) CaCl

10

1/1/0.1

5



15

Reaction time (hr)

20

25

30

300

250

200

150

100

50

0

0

Surface area (m²/g slag



Figure 5. Effect of gypsum or CaCl, on Ca2+ concentration. 92 °C; agitated; 16-21% solids. Labels indicate lime/slag/additive wt ratio.

addition of gypsum did maintain a higher concentration of Ca²⁺ overall.

The data imply that with gypsum present, only a minimal amount of lime was initially required. It is clear from Figure 4 that the experiment with 0.1/1/0.1 lime/ glass/gypsum had a very high rate of surface formation; however, at longer reaction times, the rate decreased. It is thought that the Ca²⁺ from the 0.1/1/0.1 lime/slag/gypsum recipe was depleted and beginning to limit the reaction after 22 hr. Unfortunately, the liquid filtrate, and, therefore, a measurement of solution Ca2+, was not available to support this.

X-ray data support the hypothesis that the 0.1/1/0.1 lime/slag/gypsum reaction was limited by Ca2+ after 134 m^2/g (22 hr of reaction). Figure 6 shows the diffraction patterns for a range of lime/slag/gypsum recipes. It is clear that excess hydrated lime was still present after 30 hr, and that $122 \text{ m}^2/\text{g}$ have been formed with the 0.5/1/0.1 recipe. While gypsum was present in the pattern at 3 hr for the 0.1/1/0.1 recipe, no excess lime was visible as Ca(OH)₂ at this early time, nor throughout the reaction. Results from the lime/glass/gypsum system showed that surface area would continue to form after X-ray diffraction no longer detected Ca(OH)₂.⁷ This was true in this system as well. However, it appears that the higher concentration of lime maintained the reaction for a longer time.

Taylor⁸ stated that a Ca²⁺ concentration between 1 and 20 mM is necessary to produce the C-S-H solid phase with a Ca/Si ratio of 0.8-1.5, believed to be one of the desired, high-surface-area phases. After 30 hr of reaction, the product (~139 m²/g) prepared from 0.1/1/0.1 lime/ slag/gypsum was analyzed by "selective dissolution" and found to have a Ca/Si ratio of 1.1. Increasing the lime concentration to 0.5/1/0.1 lime/slag/gypsum produced a 30-hr product with 122 m²/g and a Ca/Si ratio of 1.9. While this ratio was outside of the 0.8-1.5 range described by



Figure 6. X-ray pattern: sorbents prepared with additives. 92 °C; agitated; 20-wt % solids. 0.1/1/0.1 lime/slag/gypsum – 3 hr – 55 m²/g. 0.1/1/0.1 lime/slag/gypsum – 30 hr – 139 m²/g. 0.5/1/0.1 lime/slag/gypsum – 30 hr – 80 m²/g. 1/1/0.1 lime/slag/gypsum – 30 hr – 122 m²/g. 0.5/1 lime/slag – 50 mM CaCl₂ – 21 hr – 115 m²/g. L: Ca(OH)₂; G: gypsum (CaSO, \bullet 2H₂O).

Taylor, the X-ray diffraction pattern in Figure 6 showed this sample to have excess lime present. Therefore, the actual Ca/Si ratio of the high-surface-area solids in this sample was undetermined, and it was likely that the ratio was in fact within the 0.8–1.5 range.

Figure 6 also shows the diffraction pattern hump created by the CSH amorphous phase at ~28–33 2-theta. The patterns after 30 hr of reaction also show the smaller CSH peak at 2-theta of 50. The hump at 2-theta from 28 to 36 measured from the sample which had only 3 hr of reaction time is indicative of the glassy phase of slag. It is clear from the figure that the product phase is nearamorphous CSH. This conclusion is supported to a greater extent by Arthur.⁷ The peak at 2-theta of 11 was an anomaly that appeared in a few of the long-time slagbased sorbents. It was not identified, as it was not consistently present.

*Effect of CaCl*₂. Presuming that the results observed with the addition of gypsum were strictly a function of Ca²⁺ concentration, it seemed obvious to observe the effects of boosting the Ca²⁺ concentration with CaCl₂. Figure 4 shows the formation of surface area from slag with 50 and 90 mM of CaCl₂ in the slurry. The addition of 50 mM CaCl₂ created a product with the same surface area behavior as that created with 0.1 g gypsum/g slag. The addition of 90 mM CaCl₂ caused an unexpected upward curvature in the formation of surface area curve. This is probably due to either experimental scatter or the excessively high ionic strength of the solution slurry.

Figure 5 presents the Ca concentration data for the experiments with CaCl₂ added. The Cl⁻ experiments had

a considerably larger concentration of Ca^{2+} ; however, the surface area in Figure 4 did not increase likewise. Therefore, while a sufficient Ca^{2+} concentration must be maintained, either by the addition of gypsum or $CaCl_2$, an excess beyond the 20 mM suggested by Taylor⁸ is not necessarily beneficial.

Release of Alkali from Slag

If the rate of surface area formation is proportional to the dissolution of the slag, it might follow that it is also proportional to the dissolution of individual components of the slag. This was shown to be true for the dissolution of Na⁺ from the lime/glass system.⁷

Figure 7 shows the release of Na⁺ and K⁺ from slag for several different reactant recipes. The experiments represented in Figure 7 include various lime/slag ratios, without additives, with gypsum, and with CaCl₂. Except for a couple of outlying points that are not shown (from the 90 mM CaCl₂ experiment), the release of alkali is quite linear with surface area. Figure 7 also shows that the K⁺ and Na⁺ diffuse out from the SiO₂ matrix at proportional rates.

While it is clear that the dissolution of alkali from the SiO_2 matrix is proportional to the formation of surface area, this does not imply that the dissolution of the SiO_2 matrix is rate limiting. Rather, the rate of both processes is probably controlled by diffusion through the calcium silicate product layer.

SORBENT CHARACTERIZATION-SEM

SEM was utilized to observe overall structural characteristics of the slag sorbents. Figure 8a shows the sorbent created from lime, slag, and gypsum. In appearance, it was very similar to the solid produced from glass, lime, and gypsum.⁷

Figure 8b shows solids prepared from lime and slag with 50 mM $CaCl_2$ in solution. It is quite clear from the



Figure 7. Release of Na⁺ and K⁺ from slag during preparation. 92 °C; agitated. Experiments without additives, with gypsum, and with CaCl₂.

figure that the solids appear to have a different surface structure than those prepared with gypsum, even though the surface areas were essentially the same. X-ray patterns shown in Figure 6 failed to show any pronounced structural differences between the two solids, such as the presence of CaCl₂ precipitate. While both have excess lime present, the overall structures appeared to be that of CSH. Porosity measurements of the two solids also supported a difference in solid phase, however. While both solids had very similar surface areas (115 vs 122 m²/g), the solid sample prepared with Cl⁻ had a porosity of 0.49 compared with 0.66 cm³/g for the sample prepared with gypsum.

SO₂ Reactivity of Slag Sorbents

The goal of silicate sorbent preparation is to optimize reactivity with acid gases such as SO_2 . The SO_2 reactivity experiments with slag sorbents were conducted with a simplified synthesized flue gas consisting of only SO_2 , N_2 , and H_2O for screening purposes. A typical desulfurization application might treat a flue gas stream including O_2 , CO_2 , NO_3 , and HCl, in addition to SO_2 .

Figure 9 shows the results from reacting several slag sorbents with SO_2 in a humid gas stream at 50 °C. "Solids conversion" is defined as the cumulative moles of SO_2 removed, normalized by the total amount of initial alkalinity in the packed bed reactor. The fractional SO_2 removal was determined in 30-sec intervals by normalizing the moles of SO_2 removed during that interval, as measured in the gas phase, by the measured moles of SO_2 in the inlet. It is clear that the silicate sorbents are substantially more reactive than hydrated lime, the typical industrial sorbent. This was indicated by the sustained rate of SO_2 removal as the solids were utilized, resulting in a much higher maximum solids conversion after 1 hr of reaction. The two sorbents prepared with gypsum indicate an increased SO_2 reactivity with increasing surface area. Similar results have been published for sorbents prepared from recycled container glass.⁷

As shown earlier, sorbents prepared with $CaCl_2$, in lieu of gypsum, formed solids of very high surface area. The SEM micrographs presented in Figure 8, however, suggest that the silicates prepared with $CaCl_2$ were different than those prepared with gypsum present. Figure 9 shows that the SO₂ reactivity of sorbents prepared with $CaCl_2$ was substantially lower than that expected from the high surface area of the solids. It appeared that even though $CaCl_2$ was successful in producing a high-surfacearea product, that product was not as reactive with SO₂.

One hypothesis is that the $CaCl_2$ in the liquid solution remained in the pores of the solid after filtering and precipitated during the drying process. This precipitate has a high surface area but is not reactive toward SO_2 . The X-ray pattern of this sorbent shown in Figure 6, however, did not show any crystalline $CaCl_2$, which would be the expected precipitate. Determining the exact solid phase of the slag sorbent prepared with $CaCl_2$ was not within the scope of this project.

CONCLUSIONS

Calcium silicate solids were prepared from hydrated lime and iron blast furnace slag in an aqueous agitated slurry at 92 °C. Without additives present, the surface area of the product improved by increasing the lime/slag weight ratio to 2. At higher lime/slag ratios, the dilution effect of the excess lime caused a decrease of the product surface area. The addition of gypsum and CaCl₂ dramatically



Figure 8. SEM: calcium silicate sorbents from slag. 92 °C; agitated. (a) 0.5/1/0.1 g lime/slag/gypsum – 20% solids; 30-hr reaction time; SA = 121.5 m²/g. (b) 0.5/1 g lime/slag – 20% solids; 50 mM CaCl₂; 21-hr reaction time; SA = 114.5 m²/g.



Figure 9. SO₂ reactivity for silicate sorbents prepared from slag. 50 °C; 58% RH; ~1000-ppm SO₂. 1.521 slpm total gas rate; 0.1-g sorbent. Labels indicate lime/slag/additive wt ratio and surface area. Solids preparation: 92 °C; agitated; 20% solids.

improved the formation of high-surface-area solids. Using a 0.1/1/0.1 lime/slag/gypsum ratio produced solids with the highest absolute surface area of 139 m^2/g (167 m^2/g slag) after 30 hr of reaction. There was evidence, however, that the reaction rate was slowing due to the consumption of the hydrated lime. Increasing the lime concentration to 0.5/1/0.1 lime/slag/gypsum produced solids with 194 m²/g slag (122 m²/g), and the reaction appeared to continue past 30 hr. The silicate sorbents were consistently more reactive with SO₂ than hydrated lime, the typical commercial sorbent. The SO₂ reactivity of solids prepared with CaCl₂, in contrast to gypsum, was unexpectedly low given the high surface area. This emphasized the understanding that the surface area/SO₂ reactivity correlation is highly dependent on the solid phase. H₂O₂ was shown to be an effective additive to oxidize sulfide released from the slag during sorbent preparation.

REFERENCES

- 1. Rochelle, G.T. Discovery 1993, 13(1), 33-37.
- 2. Jozewicz, W.; Rochelle, G.T. Environ. Prog. 1986, 5(4), 219-224.
- Kind, K.K. Ph.D. Thesis, University of Texas at Austin, Austin, TX, 1994.
- Jozewicz, W.; Jorgensen, C.; Chang, J.S.; Sedman, C.B.; Brna, T.G. J. Air Pollut. Control Assoc. 1988, 38, 796-805.
 Jozewicz, W.; Gullett, B.K.; Tseng, S.C. Presented at the Second Inter-
- Jozewicz, W.; Gullett, B.K.; Tseng, S.C. Presented at the Second International Conference on Municipal Waste Combustion, Tampa, FL, April 16–19, 1991.
- Arthur, L.F.; Rochelle, G.T. *Environ. Prog.* 1998, *17*(2), 86-91.
 Arthur, L.F. Ph.D. Thesis, University of Texas at Austin, Austin, TX,
- Arthur, L.F. Ph.D. Thesis, University of Texas at Austin, Austin, TX, 1998.
- Taylor, H. *The Chemistry of Cements*; Academic: New York, 1964; Vol. 1.
- Jozewicz, W.; Chang, J. Evaluation of FGD Dry Injection Sorbents and Additives, Vol. 1: Development of High Reactivity Sorbents; EPA-600/7-89-0006a; Prepared for the U.S. Environmental Protection Agency by ACUREX Corp.: 1989.
- Koch Industries. Material Safety Data Sheet: Ground Granulated Blast-Furnace Slag; National Fire Protection Association: Washington, DC, 1980.
- Jozewicz, W.; Rochelle, G.T.; Stroud, D.E. Presented at the 1991 SO₂ Control Symposium, Washington DC, December 1991; Paper 7-12; EPRI TR-101054.
- 12. Stroud, D.E. M.S. Thesis, University of Texas at Austin, Austin, TX, 1991.
- 13. Sigma-Aldrich; H₂S Material Safety Data Sheet, 1994.
- Peterson, J.R. M.S. Thesis, University of Texas at Austin, Austin, TX, 1987.
- Peterson, J.R.; Rochelle, G.T. Environ. Sci. Technol. 1988, 22(11), 1299-1304.
- Peterson, J. Ph.D. Thesis, University of Texas at Austin, Austin, TX, 1990.
- 17. Kind, K.K.; Wasserman, P.D.; Rochelle, G.T. Environ. Sci. Technol. 1994, 28, 277-283.

About the Authors

Lia F. Brodnax, Ph.D., is an air quality engineer with the Bay Area Air Quality Management District (BAAQMD), 939 Ellis St., San Francisco, CA 94109. She was formerly with Radian International. Ms. Brodnax's maiden name was L.F. Arthur. Gary T. Rochelle, Ph.D., is the Carol and Henry Groppe Professor in Chemical Engineering and graduate advisor in Chemical Engineering, Department of Chemical Engineering, The University of Texas at Austin, Austin, TX 78712.