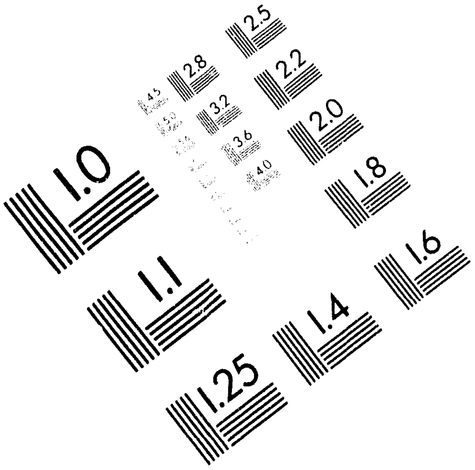

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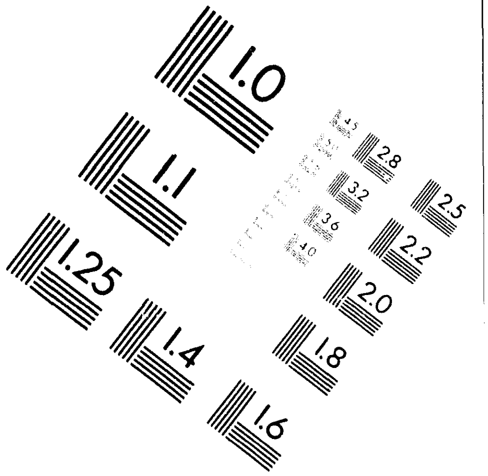

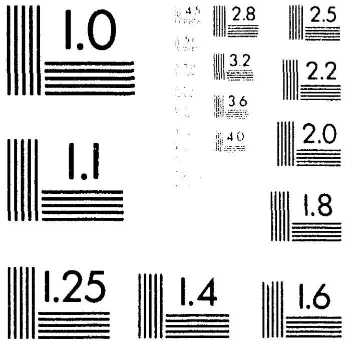

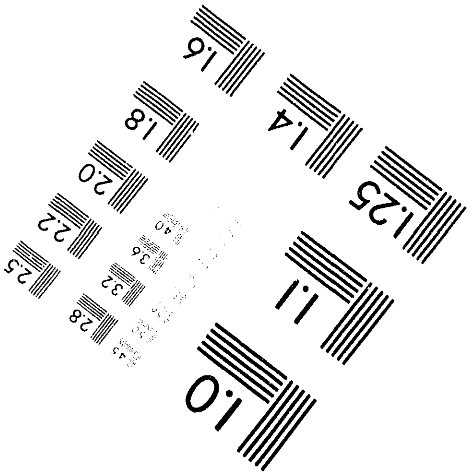

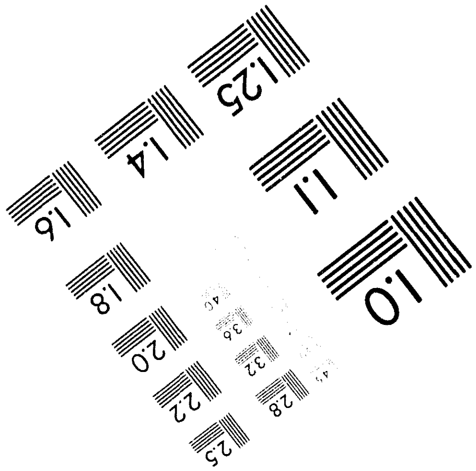

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Project Title: Effect of Sorbent Attrition on Utilization

Name of Grantee: University of Cincinnati

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FINAL REPORT

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MASTER

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EXECUTIVE SUMMARY

The overall objective of Project 1.7 for 1992-1993 was to investigate ways of using chemical attrition to improve dolomitic sorbent utilization for duct injection processes.

During this period, the project has focused on two aspects of the study that are related to the effective available sorbent recovery; 1) drop tube reactor study for the mechanisms of reaction between dolomitic sorbent and flue gas in primary duct injection and subsequent collecting processes, and 2) re-hydration study to determine the methods and factors relating to the process of hydration

A drop tube reactor system has been specially built for the project. The samples prepared from this system were used for both the study of reaction mechanism and the rehydration process. The temperature in the drop varied from 800°F to 1200°F, with sorbent residence time 1.5 sec. Studies was mainly focused on the samples prepared form the drop tube system with low particle collector temperatures in the range of 70°F to 90°F. It took about 30 minutes to prepare enough sample for one condition study. Thus the sample finally collected from filter was accumulated during this period, which was similar to what would happen in a bag house.

Carbon, hydrogen and sulfur content of all samples from drop tube system were analyzed in order to understand the reaction process. It has been observed that:

* Hydration content decreased significantly at high temperatures after primary duct injection.

* Carbonation rate for type S dolomitic lime increased with temperature, but had an extreme value for type N dolomitic lime around 1000°F.

* A sulfation window was observed around 1000 to 1100°F.

* 1100°F might be an optimum range for high sorbent usage in primary desulfurization and effective recovery of available sorbent after primary injection.

X-ray diffraction was used to identify the molecular forms of products to assist the understanding of reaction mechanism.

* The in-complete usage of sorbent in the primary injection process was evident.

* Appreciable amount of de-hydration and carbonation was observed for all samples.

* A $MgCO_3$ peak was found in the spectrum of reacted type S dolomitic lime sorbent. This might suggest that $Mg(OH)_2$ was more reactive that MgO under testing conditions. Since carbonation generally competes with desulfurization processes and reduces the amount of oxides that is essential for sorbent recovery by hydration, this tendency should be avoided.

Both atmospheric hydration and pressurized hydration were tested. It was seen that:

* Hydrogen content in the samples increased significantly for both methods.

* There were definite signs of successful hydration of MgO even though a product shell may have been formed which makes it difficult for SO_2 to diffuse through the outer sorbent particle layer.

* There were different amounts of carbonation in the hydration process, depending on the extent of contact with air.

Comparative TGA tests were performed to determine the reactivity change before and after hydration. The highest increase in reactivity after hydration treatment was observed for type n dolomitic lime at 1100°F. Recall that this was the temperature that was supposed to be the optimum range for duct injection: it not only had a high sulfation rate in primary injection, but also a low carbonation rate and a high dehydration rate. Large amounts of oxides were in the sample prepared at this drop tube temperature, providing a very good condition for making use of the hydration method to induce the fracture of spent sorbent particles.

I. INTRODUCTION

A. PROBLEM STATEMENT

It is known that one of the primary mechanisms for poor sorbent utilization lies in the fact that the products of SO_2-sorbent reactions have such large molar volumes that they plug the pores necessary for SO_2 to diffuse into the particle interior. Current measurements of the rate of reaction between SO_2 and $Ca(OH)_2$ at 1000°F by EPA indicate that 25% of the particle is converted in milliseconds, at which point the reaction essentially stops. For a spherical sorbent particle, this represents a penetration of only 9% of the initial radius of the particle. Any method that may cause the fracture of used sorbent particles will thus expose fresh un-reacted surface of sorbent and result in available sorbent recovery.

There are several mechanisms that may cause the breakage of particles.[1] External mechanical stress may be exerted on a particle and cause particle fracture when it exceeds the cohesive forces to prevent the breakage. Cracks in material are usually the weak points where fracture starts. External stress is also a very important reason for particle abrasion. Particle fracture and abrasion are the basic aspects of mechanical attrition in creating new and reactive sorbent surfaces in fluidized bed units.

Heat and pressure can also induce particle fracture. The elastic energy stored in the body of a particle at the time of fracture would be the driving force for crack propagation in thermal fracture. Pressure induced fractures are commonly coupled by heat. A particle containing a liquid or gas will generate an increase in internal pressure when the liquid or gas is heated. If the temperature change is accompanied by a phase change for either the contained liquid or gas, or even the particle's solid core, the pressure generated can be large enough to fracture the particle. The fragmentation of salt crystals during evaporation is probably due to the entrapped liquid bursting the crystal which formed around the liquid drop.

In addition, chemical reaction is also a very important factor in leading to particle fracture. When a certain material takes part in a chemical reaction, stress differences are created in the particle according to the position of the reaction. Since there are usually heat and pressure changes in chemical reactions, these three factors may work consistently. There are cases of making use of the breakage of particles in chemical reaction to create a clean, new and reactive surface to accelerate the desired reaction such as the manufacture of phosphoric acid from phosphate, where the rupture of particles helps remove the impermeable sulphate layer on the surface of the rock. In fact, the slacking of quicklime is a very good example of the comprehensive effect of chemical reaction, heat and pressure in leading to the breakage of particles. Compared to the mechanical attrition process, this can be referred to as chemical attrition.

Among many sorbents currently used in desulfurization processes, dolomitic lime may be a good candidate for use in medium temperature duct injection. Dolomites are characterized by a large portion of magnesium (instead of high calcium) in the crystal structure of common limestones. Because of the special composition of dolomitic lime and its reactions with flue gas constituents under medium temperature (600 - 1200 °F; 315 - 650 °C) duct injection conditions, a unique structure is formed for spent dolomitic particles that provides for the potential of recovering available sorbent just by hydration-induced particle fracture. By re-injecting the recovered sorbent, it is expected that a high sorbent utilization can be obtained.

B. PROJECT OBJECTIVES

This project is to study the important aspects of recovering available dolomitic sorbent by chemical attrition. Reaction mechanism of dolomitic sorbent in duct injection processes is to be investigated, since the formation of products and their radial distribution in sorbent particles determines the possibility of available sorbent recovery. The influence of temperature and sorbent residence time on subsequent collecting filters are also to be studied since they also affect the final products and structure of the used sorbent. Different methods of hydration are to be tested to develop suitable procedures for hydrating used dolomitic sorbents with reference to the hydration methods in limestone industry.

It is expected that a optimum range of primary duct injection and sorbent collecting conditions (such as temperature and residence time) can be determined, so that a high efficiency of primary desulfurization can be obtained while the final product structure are still good for available sorbent recovery by re-hydration. It is also expected that proper re-hydration procedures can be developed to ensure high reactivity of the final product, so that high utilization of sorbent can be obtained. At the improved utilization of sorbent, the chances of using Ohio coal will be increased.

II. TECHNICAL DISCUSSION

A. CRITICAL REVIEW

In this section, special characteristics of dolomitic lime as duct injection sorbent are discussed. The idea of recovering available dolomitic sorbent after duct injection is presented and previous significant results are illustrated. Factors that may affect the effective sorbent recovery are also analyzed.

Pure dolomite has a molar ratio of Mg to Ca of 1 to 1, which can be expressed as $CaMg(CO_3)_2$. It has two forms of hydrate. Type N dolomitic lime is the normally hydrated dolomitic lime, $Ca(OH)_2MgO$. Type S dolomitic lime stands for its specially hydrated form $Ca(OH)_2Mg(OH)_2$, where the special hydration process is usually accomplished by pressurization.[2]

There have been studies,[3,4,5] and cases of applications [6,7,8,9] of using dolomitic sorbent in desulfurization. There have also been reported fundamental studies for the cyclic use of dolomite in desulfurization by the process of half-calcination, sulfidation, and carbonation.[10] However, the carbonation process is not an available sorbent recovery process, but a sorbent regeneration process. Besides, it is suitable only for a high temperature range. Since MgO (the calcination product of dolomite) remains inert at high temperatures in a flue gas environment, it is sometimes even referred to as calcium based sorbent. However, the reaction mechanism for dolomitic hydroxides at a medium temperature is quite different.

The unique characteristics of dolomitic lime in in-duct injection result from the special role of magnesium compounds. Among all the possible products of reactions between dolomitic lime and flue gas constituents (i.e. CO_2, H_2O, O_2 and SO_2), magnesium compounds generally decompose at much lower temperatures than their calcium counterparts. Under flue gas conditions, there are no stable forms of $MgSO_3$, $MgCO_3$ or $Mg(OH)_2$ present at temperatures higher than 630°F, while $CaSO_3$ and $CaCO_3$ decompose at about 1380°F and 1430°F, and $Ca(OH)_2$ at about 900°F. $MgSO_4$ and $CaSO_4$ decompose at 1500°F and 2230°F, respectively,[11] much higher than the medium temperature range of duct injection. Thus the only possible product with magnesium in this temperature range is $MgSO_4$, while there may be $CaCO_3$, CaO, $CaSO_3$ and $CaSO_4$ formed as products. Based on the above understanding, the possible reactions for type N dolomitic lime in the medium temperature range can be outlined as:

Dehydration: $Ca(OH)_2MgO \text{ ---> } CaOMgO + H_2O$
Carbonation: $CaOMgO + CO_2 \text{ ---> } CaCO_3 + MgO$
or $Ca(OH)_2MgO + CO_2 \text{ ---> } CaCO_3 + MgO + H_2O$
Sulfation: $CaOMgO + SO_2 \text{ ---> } CaSO_3 + MgO$
or $Ca(OH)_2MgO + SO_2 \text{ ---> } CaSO_3 + MgO + H_2O$
$CaOMgO + (x+y)SO + 0.5(x+y)O_2 \text{ ---> } xCaSO_4 + yMgSO_4 + (1-x)CaO + (1-y)MgO$
$Ca(OH)_2MgO + SO_2 + 0.5O_2 \text{ ---> } Ca(OH)_2 + MgSO_4$
$Ca(OH)_2MgO + (x+y)SO_2 + 0.5(x+y)O_2 \text{ ---> } xCaSO_4 + yMgSO_4 + (1-x)CaO + (1-y)MgO + H_2O$

where x and y take the values of either 0 or 1. For type S dolomitic lime, dehydration of $Mg(OH)_2$ should be considered. If it is not completely dehydrated in the injection process, there will be some $Mg(OH)_2$ remaining in the used particle. However, this portion should be much lower than $Ca(OH)_2$ because of the low decomposition temperature of $Mg(OH)_2$. Due to the relatively easy diffusion of CO_2 molecules through the pores of sorbent, there is $CaCO_3$ formed must be large amounts of MgO left in the un-reacted cores, together with certain portions of CaO which is shown in Figure 1.

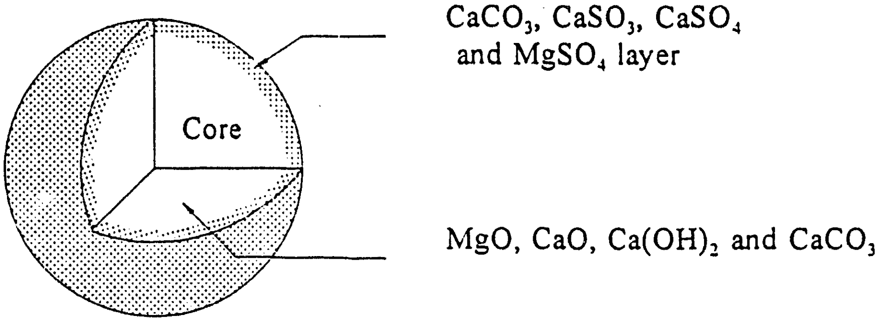


Figure 1. Dolomitic lime particle structure after in-duct scrubbing

Hydration is the method that is proposed to recover the available lime. By hydrating the oxides, it is expected that the stress created by the expansion of molar volumes in forming $Mg(OH)_2$ and $Ca(OH)_2$ will cause the fracture of used sorbent particles so as to expose the available sorbent inside. This basic idea is illustrated in Figure 2. The mechanisms of heat and pressure induced particle fracture may also be used to enhance this process.

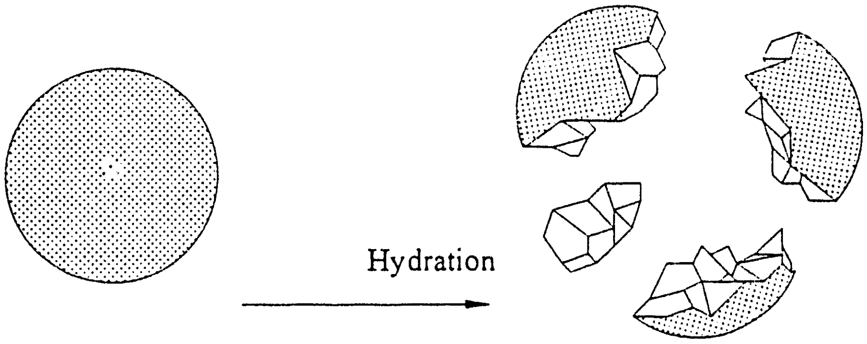


Figure 2. Induction of Particle Fracture by molar volume expansion in hydration

The possibility of re-hydrating used sorbents after primary duct injection processes was tested in the previous year with a fixed bed reactor. The reactant gas concentrations were 14% CO_2, 2500ppm SO_2, 3% O_2, 8% H_2O and balance N_2. Dolomitic lime samples were kept in the bed at a controlled temperature for 20 minutes before they were collected for the hydration operation. A Du-Point TGA was used to compare the reactivity of used sorbent before and after hydration by controlling the temperature and gas concentrations to those in the fixed bed. Comparisons were made on a fixed MgO-CaO weight bases. The type S dolomitic lime sample that was prepared under 1200°F showed significant increases in reactivity after hydration as shown in Figure 3.

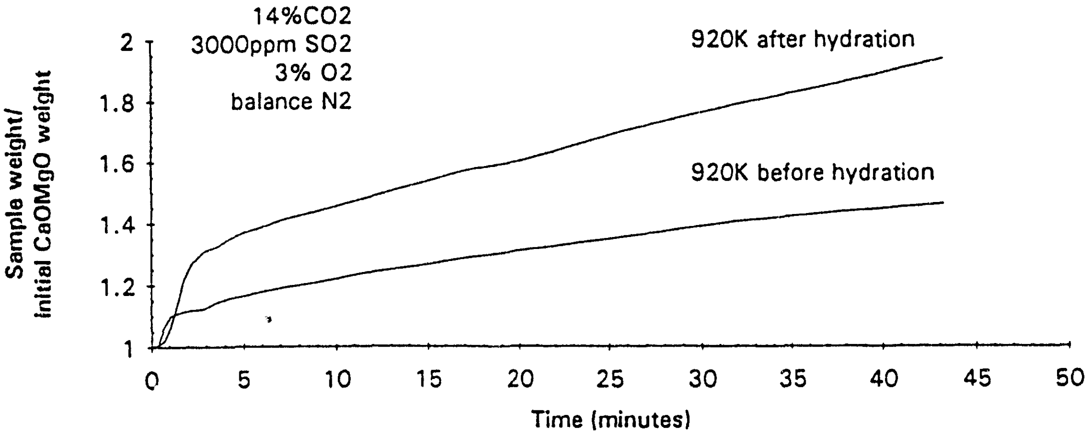


Figure 3. Increase in used sorbent reactivity after atmospheric pressure hydration for type S dolomitic lime at 1200°F

Not much increase in sorbent utilization by hydration was observed at lower temperatures. A sample which was prepared under 800°F was selected to test reactivity under 1200°F without hydration. The result is shown in Figure 4. Higher sorbent utilization was observed at 1200°F compared to the results on the same sample at a temperature of 800°F Thus, it is understandable that at low temperatures when reaction rates are low and sorbent is not fully utilized, hydration shows no effect on sorbent utilization. It can also be inferred from the above fact that the effect of available sorbent recovery is a function of the extent of its primary usage.

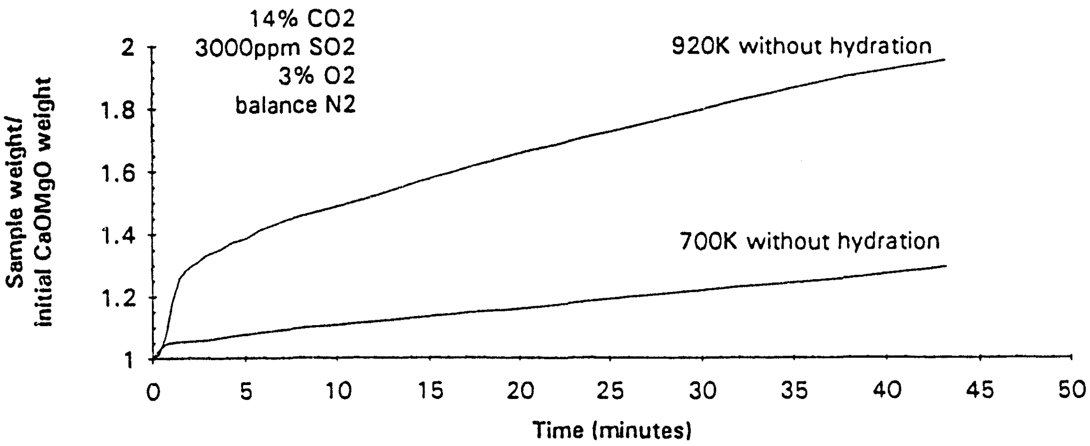


Figure 4. Increase in sorbent utilization due to the increase in reaction rate type S dolomitic lime primarily reacted under 800°F

It is obvious that the effect of sorbent recovery depends on the extent of each reaction and the final product distribution inside sorbent particles. In fact, dehydration, carbonation and sulfation reactions happen simultaneously in duct injection process. Since reaction rates change differently with temperature, the extent of each reaction varies with temperature and concentration of flue gas constituents. Thus, the temperature and reactant gas concentrations at which samples are prepared will strongly affect the efficiency and conditions for sorbent recovery.

The temperature and concentration effects on final sorbent structure result from not only the conditions in the duct at which the sorbent is injected, but also the conditions at the sorbent collector. Because of the long residence time in particulate collectors, some reactions may proceed to a considerable extent even though the reaction rates have been lowered due to lower temperatures and the reduced diffusion velocity of reactant gases due to the formation of product layers. This 'bag house effect' will have significant influence on the recovery of available layers. This 'bag house effect' will have significant influence on the recovery of available sorbent.

If the temperature at the collector is below about 400°F (and above the saturation temperature of water in the flue gas), the reaction rates for each reaction are low. However there are tendencies of forming all kinds of compounds including $MgSO_3$, $Mg(OH)_2$, $MgCO_3$ and $Ca(OH)_2$, which will tend to reduce the amount of oxides that are necessary for the effective hydration process in order to break the particles. Carbonation process may be more obvious than the sulfation because of the smaller molecular volume and easy diffusion of CO_2. Long residence times at these temperatures may be an unfavorable condition for sorbent recovery.

If the particle collecting temperature is in the range of about 450°F to 600°F, no $MgSO_3$ will be formed. If the original sorbent is type S dolomitic lime, decomposition of $Mg(OH)_2$ will proceed if there is any remaining from the duct injection process, which is favorable for the subsequent sorbent recovery process. While at the same time, carbonation rates of both magnesium and calcium will be increased due to the higher temperature as compared to the above low collector temperature case.

If the collector temperature is above 650°F, little or no $MgCO_3$ will be formed; magnesium will be all in its oxide form except for the product $MgSO_4$. This condition is most favorable for sorbent recovery since the particles will contain substantial percentages of MgO ready for hydration. However, the carbonation rate of calcium may be the highest at this temperature. The effective portion of CaO will be reduced.

In all these cases, the appropriate collector temperature and suitable residence time of particles needs to be studied in order to find out the optimum conditions for sorbent recovery.

Another important aspect related to effective sorbent recovery is the method and condition for hydration. For common quicklime, high calcium quick lime completely hydrates into a hydroxide within minutes to a hour without much difficulty. But this does not occur with dolomitic quicklime. Very few can be substantially hydrated in any practical length of time under atmospheric pressure except retained in silos steeped in excess water.

Consequently, most normal dolomitic hydrates contain a paucity of $Mg(OH)_2$, and has the form of $Ca(OH)_2MgO$. However by subjecting the dolomitic quicklime to pressure and high temperature, all or most of the MgO may be hydrated. This is the commercial way of producing type S dolomitic lime. Usually pressure varies form 25psi to 100psi. Generally, 80psi is frequently employed. Higher temperatures are also stimulated by the pressure (250-400°F), much higher than in atmospheric hydration plants.

The extent and rate of hydration are sensitive to a number of factors.[2] The varying rates and divergent physical properties of hydrates are directly related to its derivative quicklime. Slight deviations in hydration conditions may exert a marked effect on rate of reaction. Generally, high chemical purity results in rapid hydration. The greater the percent of impurities, the slower the rate. Pores are clogged, and the surface is partially coated with a slag formed by lime fluxing of such impurities as silica, alumina, and iron, rendering it more impervious to the entrance of water. Increments of MgO have a retarding effect on the rate of reaction, a very impure dolomitic lime would be the slowest, almost impossible to hydrate. Fine and dust like particles may increase the rate. The rate accelerates with increasing temperature and may reach its peak with many limes when reacted with steam. Increase the amount of water retards the rate of hydration and mutes the heat evolved in the diluted mixture. Agitation of the lime and water increases the rate and dispersion of the lime particles markedly. The quality of slacking water also has an effect on hydration. High sulfate content water has been reported to exert pronounced retardation on hydration and reduce hydrate yield. Carbonation reactions interfere with the hydration process. A partially stir slaked or re-carbonated quicklime hydrates sluggishly. Usually industrial hydration processes are carried out in a closed system to prevent interference from ambient CO_2.

Various methods of hydration along with divergent qualities of quicklime yield hydrates of varying particle size and surface area, which affect the quality and utility of the product. Fine particles are desirable for duct injection processes for the ease of mixing the particles in the flue gas. Generally, wet hydrates with large excess water yield finer particles than dry hydrates with strictly controlled excess water. Generally agitation and increasing temperature are advantageous to employ. A few companies use an explosion method for discharging the dolomitic hydrates from the autoclave through a small pipe into a cyclone collector. The explosive ejection of the lime dries it and markedly decreases its particle size, a large percentage of which is sub-micron. In addition to the above procedures in manufacture, mechanical air separators of the centrifugal type that are conical with a hopper bottom are virtually universally employed in the final milling of the hydrate to classify the material to a fine state of subdivision.

Usually fine hydrate particles have good reactivity. But the most reliable criterion on reactivity is surface area. Tests have indicated that the adjustments in hydration practice can markedly alter the surface area. Air slaking produces the lowest surface area. Specific surfaces very less with changes in water temperature at low water-lime ratios and with water at high temperatures for all water-lime ratios. Low specific surface can be obtained with reactive soft-burned quick limes by hydrating at low water temperatures (40-55°F) with high water ratios of 18-25:1. Such hydrates will react like those derived from hard-burned limes. If a maximum surface area is desired, there is an optimum slaking water temperature and water ratio that can be empirically established for any lime. However these conditions may not be suitable for the re-hydration of used dolomitic lime. Sorbents may also exhibit quite different characteristics because of different origins or different reaction conditions. Tests should also be performed before making conclusions on a certain kind of hydration method.

B. RESEARCH STRATEGY

Based on the above analysis and the project objectives, a general approach for this project is established and is illustrated in Figure 5. A drop tube reactor is specially built for this study as will be described later. It serves for two main purposes, the reaction mechanism study and the preparation of pre-reacted dolomitic sample for re-hydration study. At step A dolomitic lime sorbent is injected into the drop tube reactor, where constant temperature and simulated flue gas flow rate are maintained. Reaction mechanism study at step B takes a portion of the reacted sample from the drop tube and perform elemental and crystal analysis. The elemental analysis at step E provides the weight content of carbon, hydration and total sulfur in the collected sample, which are good indications of the extent of carbonation, hydration/dehydration and sulfation reactions. X-ray diffraction analysis at step F helps to identify the form of existence of all elements involved in the desulfurization reaction, which, in turn, helps to clarify the reaction mechanism.

TGA test on further reactivity of the reacted sample is performed in step C to establish a reference value of weight increase, so that the reactivity of the sample after hydration can be compared to. In fact, the elemental analysis result in step E also serve as references, so that the changes in the amount of carbon, hydration and sulfur after hydration can be analyzed.

Hydration processes are performed under different pressures, the atmospheric hydration in step G and pressurized hydration in step H. For each of the re-hydrated sample, carbon, hydrogen and sulfur contents are analyzed in step I and step K. When compared to the result in step E, information about the carbonation happened in the hydration process, the extent of hydration and sulfur balance in the hydration can be obtained.

TGA tests on further reactivity are performed after both atmospheric and pressurized hydration in step J and step L. When these are compared to the result in step C, indication on the potential of increasing sorbent utilization can be obtained.

C. DROP TUBE REACTOR SYSTEM

Preparing reacted dolomitic sample that best resembles used sorbent from duct injection is crucial in both mechanism study and rehydration study. The fixed bed sulfation system used

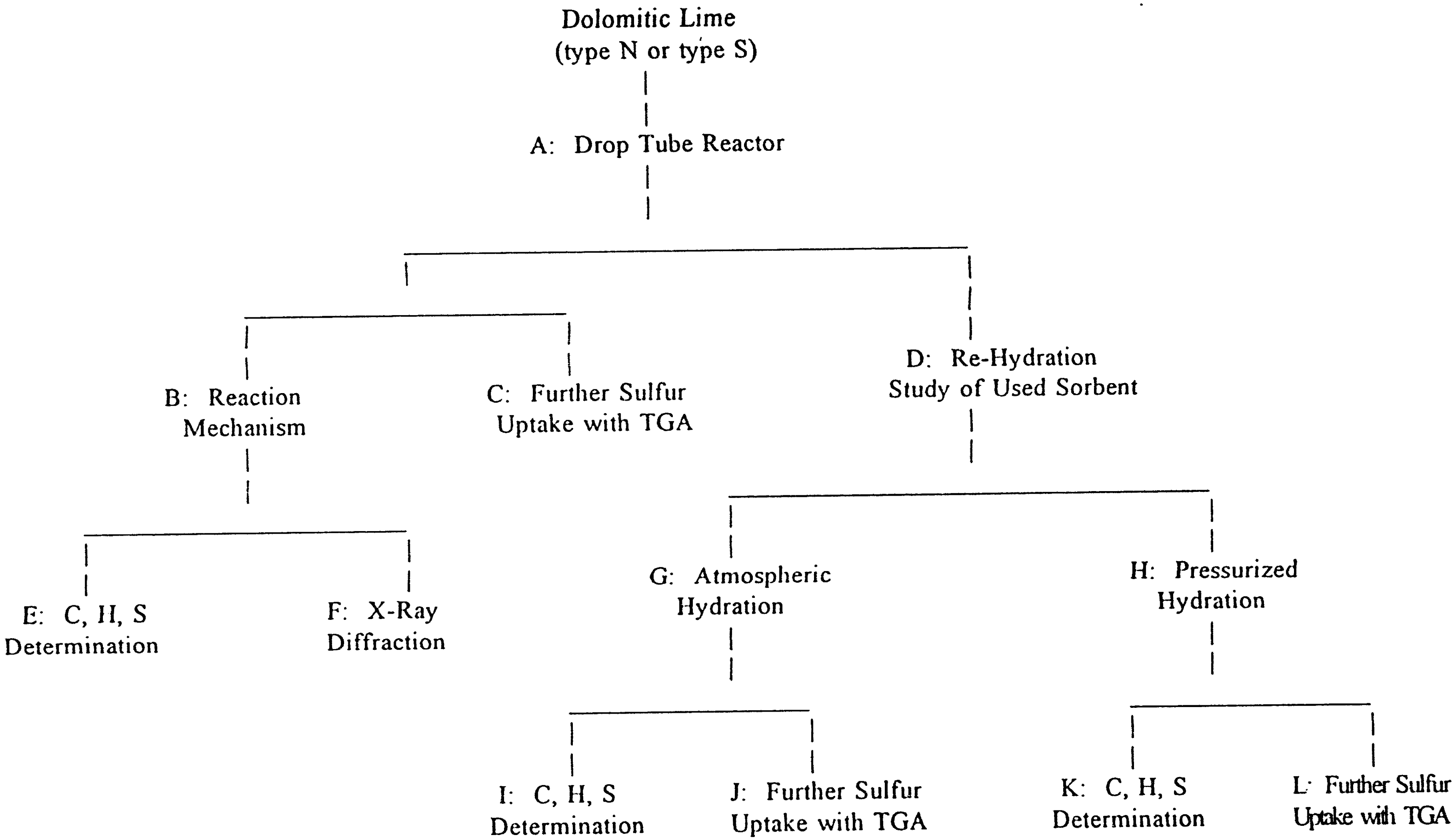


Figure 5. Illustration of the general approach

in the previous year had the problem of yielding non-uniformly sulfated sample and might have the adverse effect of thermal sintering because of the long residence time required. The newly built system is to minimize these problems while providing greater operability for further study and improvement.

I. System Description

The drop tube reactor system is shown in Figure 6. It consists of six basic units: (1) water injection unit with mixture gas preheating furnace; (2) sample feeder with its gas pre-heater; (3) mixing unit for particle and reaction gases; (4) reaction chamber; (5) sample collector and, (6) exhaust fan.

The preheating furnace is used to bring the temperature of reaction gases (SO_2, CO_2 O_2 and N_2) to about 550°F. Controlled heating from the furnace and heating tapes ensures the injection of water into the reaction gas stream without condensation and helps to maintain a constant and uniform temperature distribution in the reactor chamber. However, in order that the reactions will not take place under unexpected temperatures outside the reaction chamber, it is preferable to control the temperature of the mixture gas under 600°F when it meets with sorbent particles. This maximum temperature is obtained from previous TGA test results.

Sorbent particles are fed in by a specially made particle dispenser as shown in Figure 7. Proper amount of dolomitic sorbent will be first put into the sample holder then fed into the vertical tube uniformly by turning the auger at a proper speed. By controlling the gas flow rate in the vertical tube, particles under certain size will be entrained and carried into the reaction chamber. Agglomerates may present because of moisture according to previous tests. A throttle is designed to create high velocity gas flow to break any possible big agglomerates and fluidize all sorbent particles. In addition, nitrogen is preheated to reduce the adverse effect of moisture. However, in order to minimize the structure change in sorbent particles, the temperature of gas from gas pre-heater needs also to be controlled. The heating tapes right above the sample feeder helps to slightly increase the temperature of the particle entrained gas flow. Since gas velocity

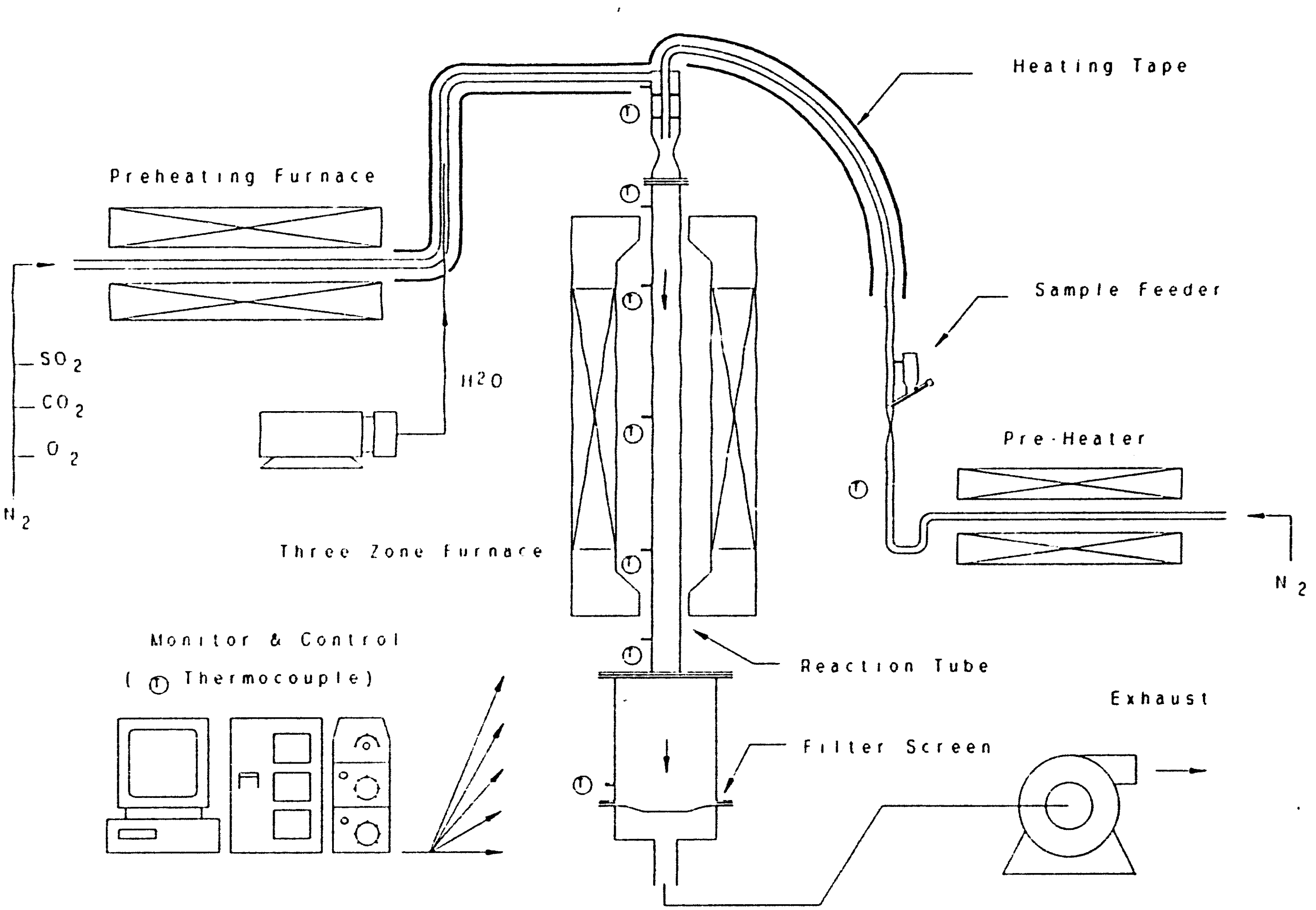


Figure 6. The drop tube reactor system

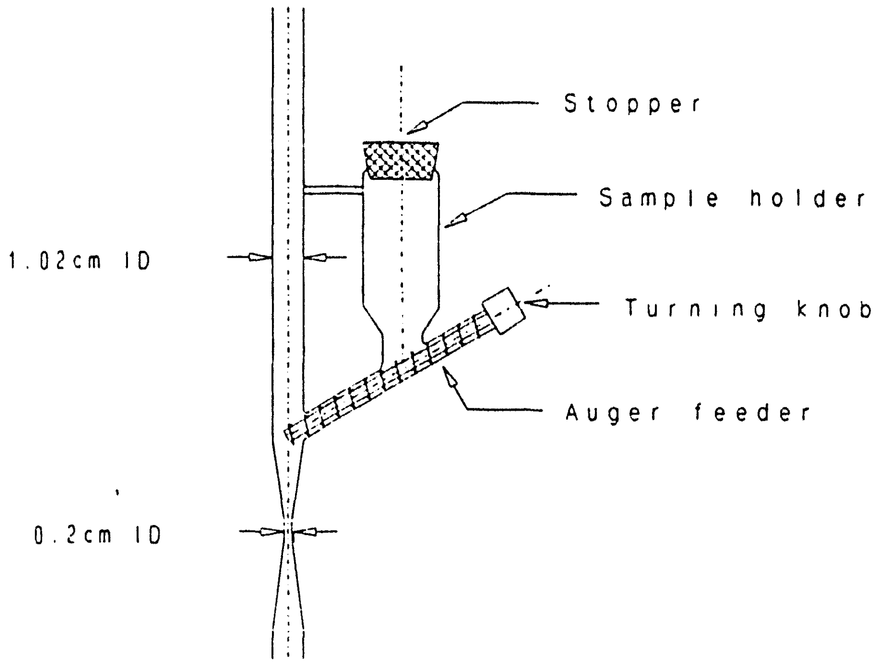


Figure 7. Drop tube reactor sample feeder

will be increased at higher temperature for the same flow rate, particles will be well carried into the mixing unit without falling back into the feeder.

A venturi is designed to mix reaction gases with sorbent particles. Two gas dispensers are used to pre-mix reaction gases and the injected water. At the same time, spatially uniform flow of the mixture gas down-stream to the venturi is obtained after the 90° bending at the manifold. When this flow is mixed with entrained particle flow and passed through the venturi throttle, it is expected that spatially uniform mixing of particles and reaction gases is obtained. Since reaction gases (SO_2, CO_2, O_2, N_2 and H_2O) and sorbent particles are mixed in this very manner, it very easy to adjust either any kind of reaction gas constituent or sorbent feeding rate, which, in turn, provides great capability in further study.

Then the well-mixed particle-gas flow enters the reaction zone downstream of the mixing venturi. The reaction chamber is encompassed by a Lindberg three zone furnace. Three separate heating zones are used to maintain a constant temperature distribution throughout the reaction chamber. Since only particles under certain small sizes will be entrained into the reaction chamber, there is not much diffusion resistance for the initial stage of reactions between these individual particles and simulated flue gas constituents. Thus, high initial stage reaction rates and relatively uniform sulfation among particles can be expected.

Finally the sulfated sorbent particles are captured on a filter downstream of the reaction tube. According to previous tests on another system, the mixed flow from reaction chamber will rapidly drop to below about 600°F when it reaches the filter. There will virtually be no further reaction proceeding on the filter at such low temperatures. Samples collected this way resemble duct injection process followed by low temperature particulate control devices. However, there is an option to keep higher temperature at the filter or even heat it up to desired temperatures. In this way particles deposited on the filter will have longer residence time to react with flue gas constituents even though at lower temperatures than in the reaction chamber and with greater diffusion resistance. Samples collected this way will have the characteristics of sorbent samples collected from warm bag house right after duct injection. Thus, it is conceivable that the samples prepared in this system resemble that from real duct injection process much better than what were obtained from fixed bed sulfation system.

The final stage of the reaction system is the exhaust pump. It is used to form a push-pull system to compensate the pressure drop in the system. The reaction chamber is expected to operate under pressure that is slightly lower than atmospheric pressure. In this way, adverse effects of back pressure at the auger of the sample feeder can be avoided.

II. Operating Criteria

a). Reaction Chamber:

Some of the principle operating conditions are listed below:

Height of Reaction Chamber: $H = 2$ ft $= 60.96$ cm
Diameter of Reaction Chamber: $D = 2.069$ inches $= 5.26$ cm
Residence Time: $T = 1.5$ sec

Thus,

Total Flow Rate: $Q_T = 883$ cm^3/sec
Velocity in Reaction Chamber: $V_R = 40.64$ cm/sec
Reaction Temperature: 800°F ~ 1200°F
Renold Number in Tube: $Re_{800F} = 316$
$Re_{1200F} = 198$

Renold numbers are far below 2100, flow is in laminar developing region.

b). Sample Feeder:

The flow velocity to fluidize individual particles under temperature 250°C (482°F) are listed in Table 1.

Table 1. Settling Velocity under 250°C (482°F)

Particle Size d_p (um)	10	40	100	100	1000
Density P_p^* (g/cm^3)	3.5	3.5	3.5	0.56	0.56
Velocity V_{TS} (cm/sec)	0.71	11.3	21.7	11.3	108.5

* Note: two densities are used to estimate solid particle and possible agglomerates

V_{TS} = 100 cm/sec is selected as the velocity in feeder section with tube diameter D_F = 1.02 cm in the following calculation. When the throttle diameter size is selected as 0.2 cm, flow velocity through throttle would be 26.0 meters/sec.

Flow through feeder: Q_{feeder} = 81.7 cm^3/sec (482°F)
Portion in total flow: 12.4 % (800°F) -- 17.5 % (1200°F)

Suppose 3000ppm SO_2 in gas flow, 1/4 of the sulfur is effectively used in sulfating sample and 25% of sorbent is practically sulfated in reaction chamber (indicating 6~7 % total sulfur content in collected sample). Then the dolomitic particle feeding rate can be estimated as:

800°F reaction chamber: 2.4 mg/sec (0.144 g/min)
1200°F reaction chamber: 2.0 mg/sec (0.12 g/min)

5 grams of sample take about 40 minutes to prepare.

c). Collecting Filter:

Effective collecting surface diameter: 17.8cm (7 inches)

Estimating according to bulk density: 0.56 grams/cm^3

Total volume for 5 grams of sample should be: 8.93 cm^3

Average thickness on filter: 0.036cm

Face velocity through filter at 600°F: 2.99 cm/sec (800°F Chamber)

2.27 cm/sec (1200°F Chamber)

D. DROP TUBE REACTOR STUDIES

Both type N and type S dolomitic lime were injected into the drop tube reactor. The particle collector filter was kept at low temperature range (122-220°F), at which even magnesium compounds such as $MgSO_3$, $MgCO_3$ and $Mg(OH)_2$ might exist as stable products. The samples thus obtained represented the comprehensive effects of both the reactions in the drop tube at certain injection temperature and the subsequent reactions on the collecting filter. Since the conditions on collecting filter were almost the same for each sample prepared for this study, the differences in data mainly represented the effects of conditions in the drop tube.

Inlet reactant gas concentrations were all kept the same for all these tests. They were 2500 ppm SO_2, 3% O_2, 8% H_2O, 14% CO_2 and balance N_2. The residence time of sorbent particles in the drop tube reaction chamber was about 1.5 seconds. Five reaction chamber temperatures were used: 800°F, 900°F, 1000°F, 1100°F and 1200°F. Compressed air was passed through the drop tube reactor in order to adjust the temperature from one level to another. After the system reached the expected constant temperature distribution, reactant gases were switched in and dolomitic lime samples were loaded into the sample feeder. By controlling the speed of the auger on the feeder, samples were fed into the reaction chamber at the rate of about 170 mg/min. Compared to the reactant gas flow rate in the chamber, this feeding rate is equivalent to 75% excess reactant gas as of SO_2 at half sorbent utilization, thus good reaction environment for the particles was ensured. It took about 30 minutes to get about 5 grams of post-injected dolomitic particles. Particles were accumulating on the collecting filter during this time. Reactions might still take place during this period at low filter temperatures and the extent of these reaction on particles were different due to the different residence time there. Therefore, samples collected from the filter were well mixed before conducting elemental analysis and further hydration tests.

The elemental analysis result of carbon, hydrogen and sulfur content for type N and type S dolomitic lime are shown in Table 2 and Table 3, respectively.

Table 2. Analytical data for type N dolomitic samples after drop tube reaction

Sample preparing conditions			Temperature (°F)				
		Blank*	800	900	1000	1100	1200
After duct injection before hydration (% by weight)	H	2.02	1.42	1.22	0.16	0.45	0.69
	C	0.72	1.87	2.86	5.73	4.80	4.75
	S	--	2.98	2.61	4.11	4.15	2.35
	TGA	1.59	1.14	1.13	1.06	1.36	1.48

Note: * The type N blank sample was not injected into the drop tube reactor, the data listed under "after duct injection" was the analytical results for the original dolomitic lime.

** TGA terms are the weight increase ratio of 1 hour weight to initial weight, not in " %". Time was counted from the moment when reactant gas was switched in. Detailed discussion follows later

Table 3. Analytical data for type S dolomitic samples after drop tube reaction

Sample preparing conditions			Temperature (°F)				
		Blank*	800	900	1000	1100	1200
After duct injection before hydration (% by weight)	H	2.88	2.30	1.68	0.98	1.45	0.62
	C	0.76	1.53	2.64	4.47	3.97	5.69
	S	--	2.31	3.77	4.03	2.28	3.08
	TGA	1.67	1.15	1.13	1.13	1.49	1.63

Note: * The type S blank sample was not injected into the drop tube reactor, the data listed under "after duct injection" was the analytical results for the original dolomitic lime.

** TGA terms are the weight increase ratio of 1 hour weight to initial weight, not in " %". Time was counted from the moment when reactant gas was switched in. Detailed discussion follows later.

Based on Table 2 and Table 3, the content of hydrogen after primary injection was plotted in Figure 8 for both type N and type S dolomitic sorbent. The hydrogen contents of the original samples were also shown as type N and type S blank for comparison purposes. It was seen that the extent of dehydration increased as temperature increased from 800°F to 1100°F. There was a doubtful value for type S dolomitic sorbent dehydration at 1100°F, since the sample feeding rate was high for this sample (about twice the usual rate). There might not be sufficient chance for it to fully react. This could also be seen on the subsequent analysis on the extent of carbonation and sulfation. 1100°F was an extreme point for dehydration of type N dolomitic lime. Besides, both type N and type S dolomitic lime dehydrated to an appreciable extent at 1200°F.

The extent of carbonation in the primary injection process was shown in Figure 9. The original carbon contents in type N and type S dolomitic lime were almost the same on this chart. It was seen that the value at 1100°F for type S dolomitic lime might be resulted from an insufficiently reacted sample. Other than that, type S dolomitic lime showed an increased tendency of carbonation as temperature increased. For type N dolomitic lime, an extreme value of carbonation occurred at 1000°F. Beyond this extreme value, the extent of carbonation decreased slightly with increased temperature.

The extent of sulfation after primary injection was shown in Figure 10. Again, the value for type S dolomitic sorbent at 1100°F showed a sign of insufficient reaction. It was supposed that there should be a sulfation window between 900°F and 1100°F for type S dolomitic lime. It was seen that the sulfation hump for type N dolomitic lime occurred between 1000°F and 1100°F.

Usually, carbonation process competes for sorbent with sulfation reaction. In addition, for the purpose of effective available sorbent recovery, large amount of oxides are needed in the spent sorbent particles. Thus, carbonation has adverse effects on both desulfurization and available sorbent recovery. Temperature range with low carbonation rate is preferred. Since the sulfation hump was between 1000°F and 1100°F for type N dolomitic lime, the extreme point for dehydration was at 1100°F and the extreme point for its carbonation was at 1000°F, it is supposed that temperature around 1100°F might be an optimum range for high sorbent usage in primary desulfurization and effective recovery of available sorbent after primary injection.

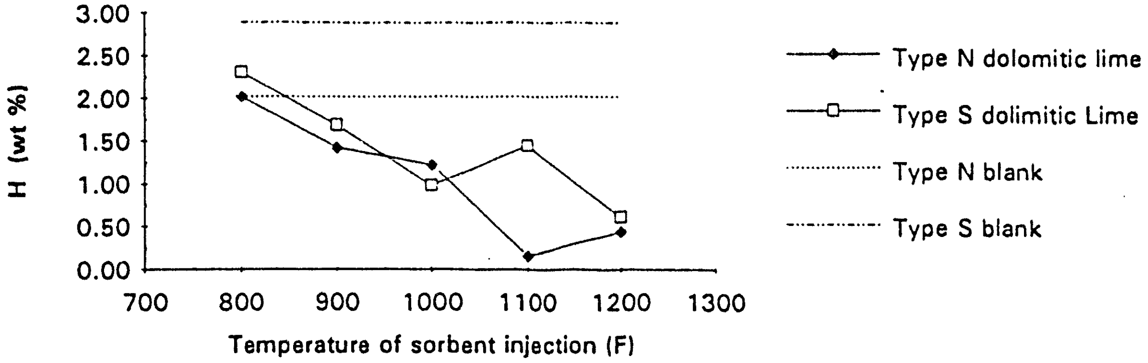


Figure 8. Hydrogen content in samples after primary injection

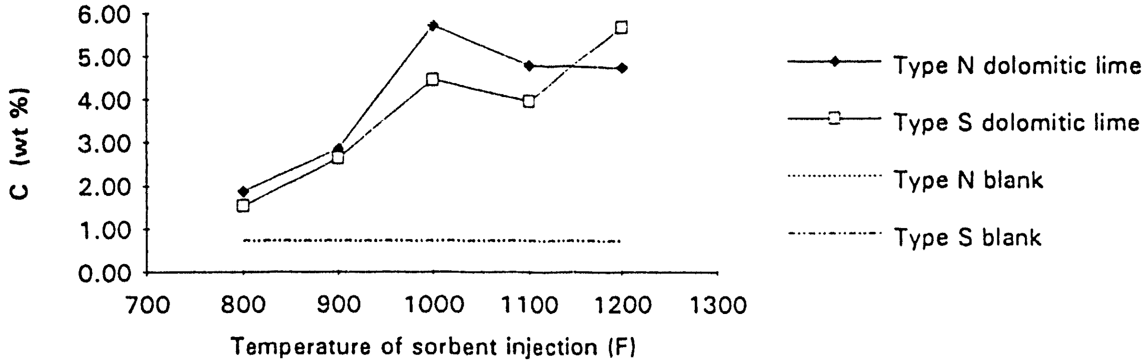


Figure 9. Carbon content in samples after primary injection

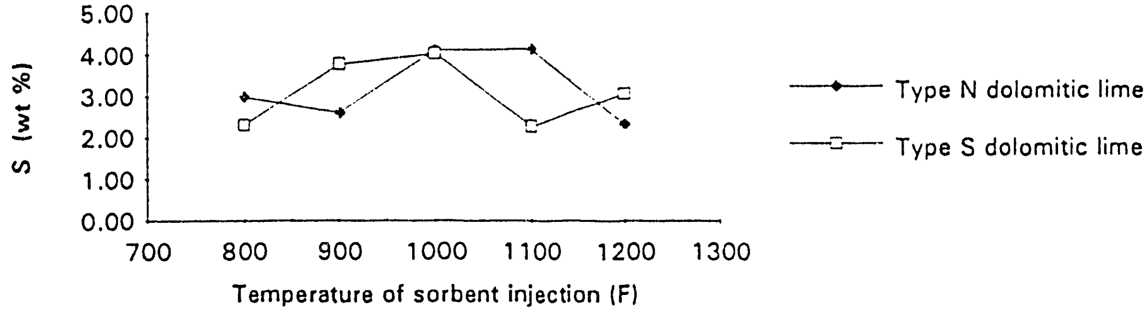


Figure 10. Sulfur content in samples after primary injection

E. X-RAY DIFFRACTION ANALYSIS

X-ray diffraction analysis were conducted to assist the understanding of the reactions between dolomitic lime and flue gas constituents in duct injection processes.

Four peaks of type N dolomitic lime were observed as shown in Figure 11. They were at 2θ angle of 18.0, 28.7, 29.4 and 34.0. In Comparison, the peaks of $Ca(OH)_2$ were shown in Figure 12. Three peaks were repeated. They were at 2θ of 18.0, 28.7 and 34.0. The small peak of 29.4 on Figure 11 was not seen here. In stead, there was a new peak occurred at 32.5. The three peaks occurred in both type N dolomitic lime and $Ca(OH)_2$ were the only peaks for CaO in the range of angle tested as shown in Figure 13, indicating the close relationship among dolomitic lime, calcium hydroxide and calcium oxide. Nevertheless, there were differences in the height (count) and widths of the corresponding peaks.

In order to help analyzing the final products, laboratory reagent $CaSO_3$ peaks were tested and shown in Figure 14, $CaSO_4$+$2H_2O$ peaks in Figure 15. The main peaks for $CaSO_3$ were 2θ of 15.9, 16.6, 23.4, 28.3 and 34.2. The main peaks for $CaSO_4$+$2H_2O$ were at 11.7, 20.8, 23.5 and 29.2.

No significant peaks for MgO was observed in this diffraction angle range as shown in Figure 16. Even though there seemed to have lots of peaks there, they were actually of really low count number on the vertical axis. Significant peaks for MgO should appear in the 2θ range of 36 to 72.

The peaks for $Mg(OH)_2$ tested were shown in Figure 17. There were only two significant peaks. The first one occurred at 2θ of 18.5. This angle was close to the peaks for CaO and $Ca(OH)_2$ at 18.0, but slightly shifted to the left. The second peak occurred at 2θ of 32.8 with much lower count than the first one.

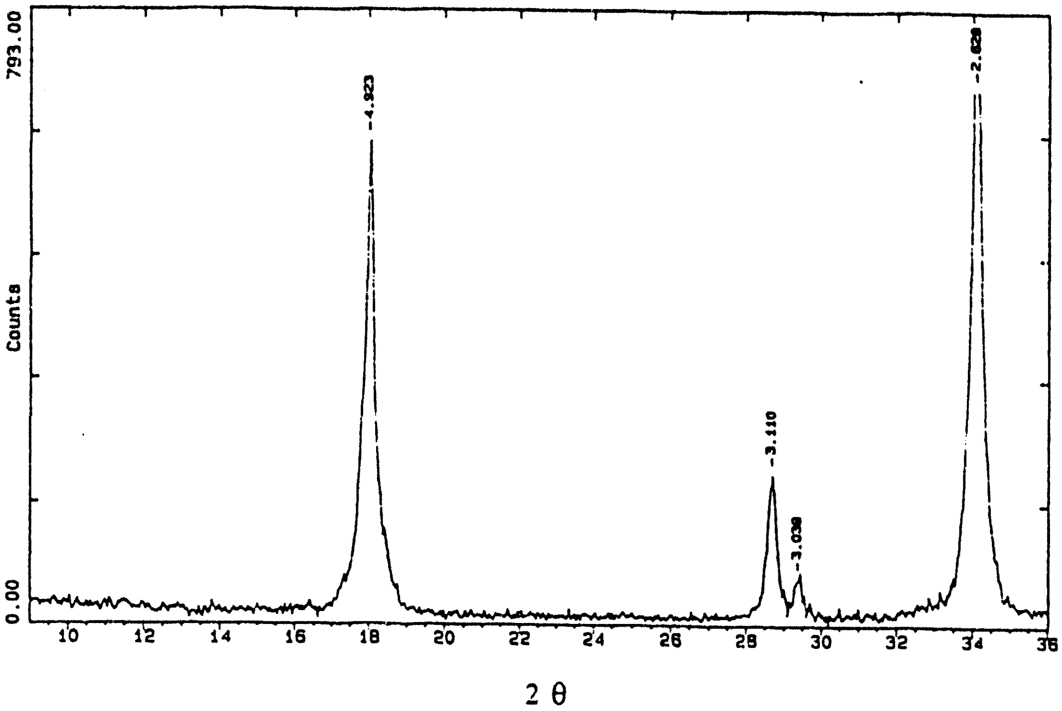


Figure 11. X-ray diffraction of type N dolomitic lime

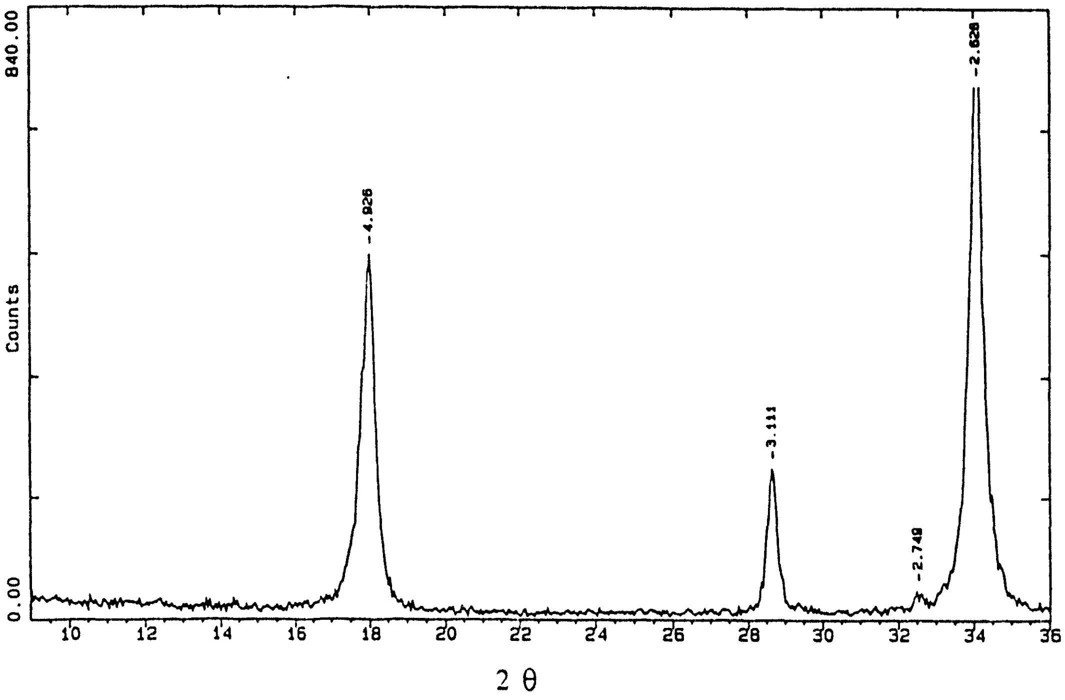


Figure 12. X-ray diffraction of $Ca(OH)_2$

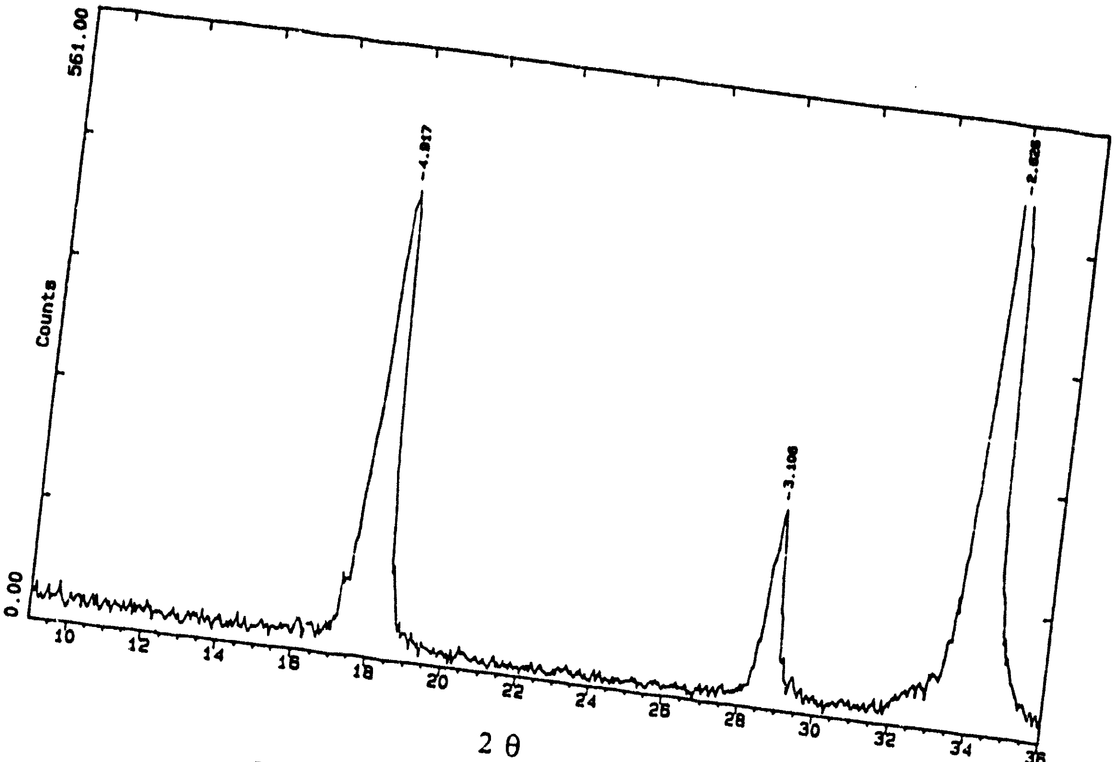


Figure 13. X-ray diffraction of CaO

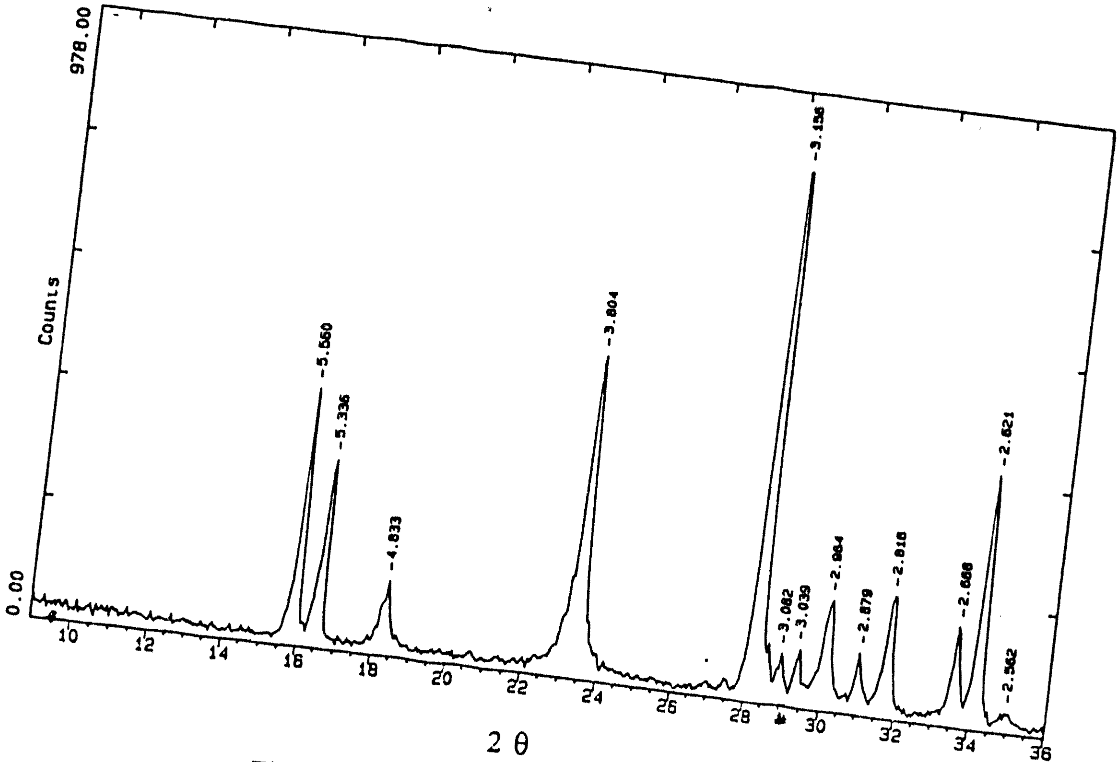


Figure 14. X-ray diffraction of $CaSO_3$

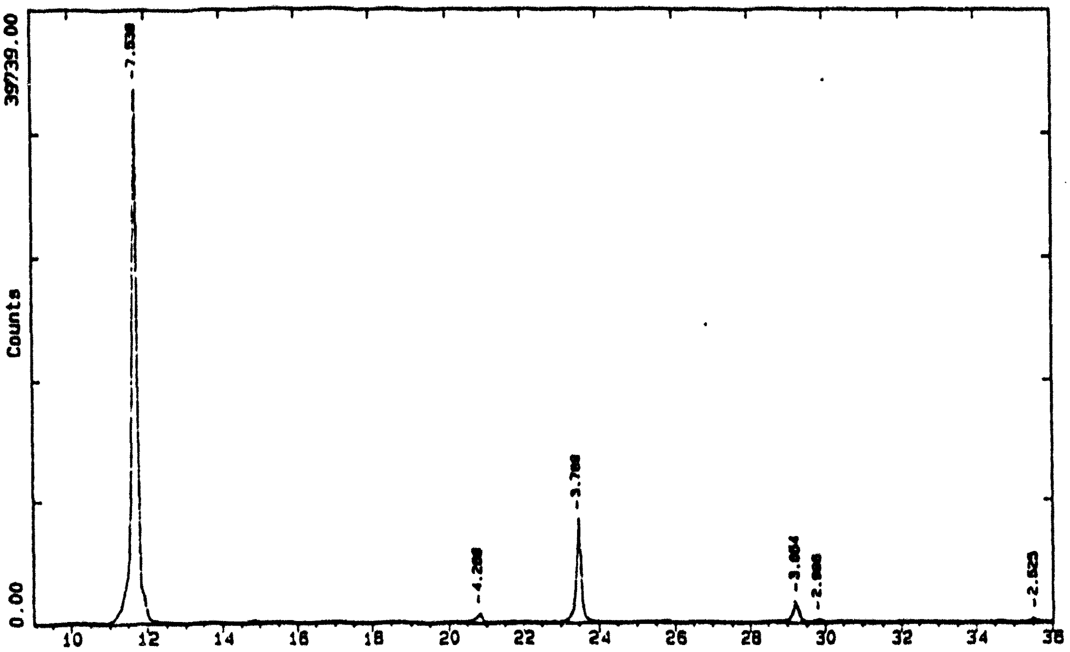


Figure 15. X-ray diffraction of $CaSO_4$+$2H_2O$

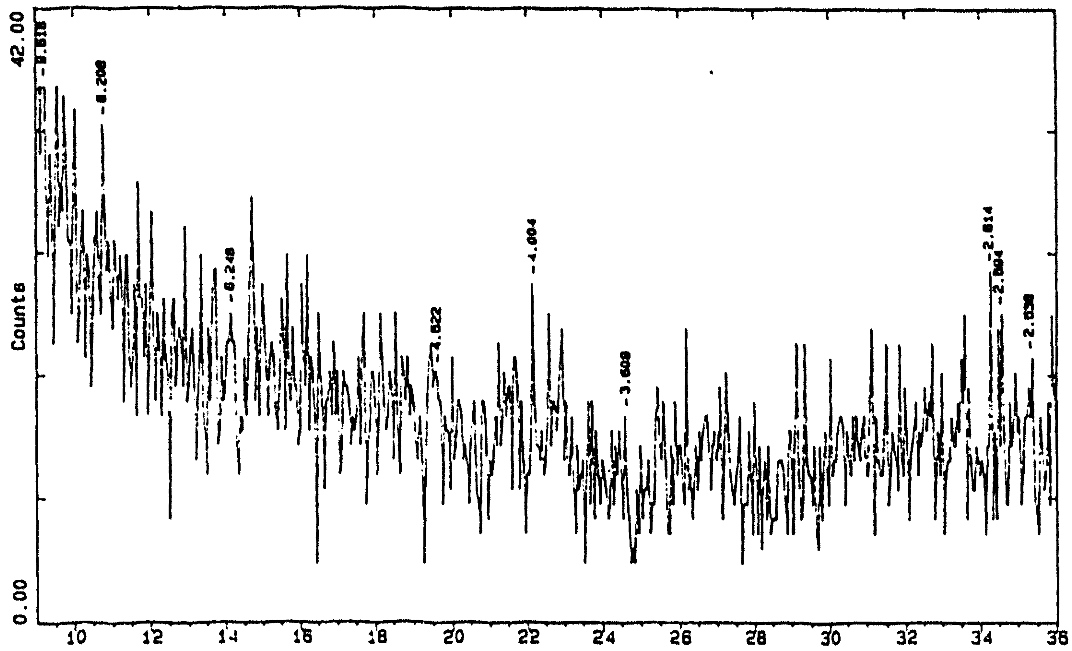


Figure 16. X-ray diffraction of MgO

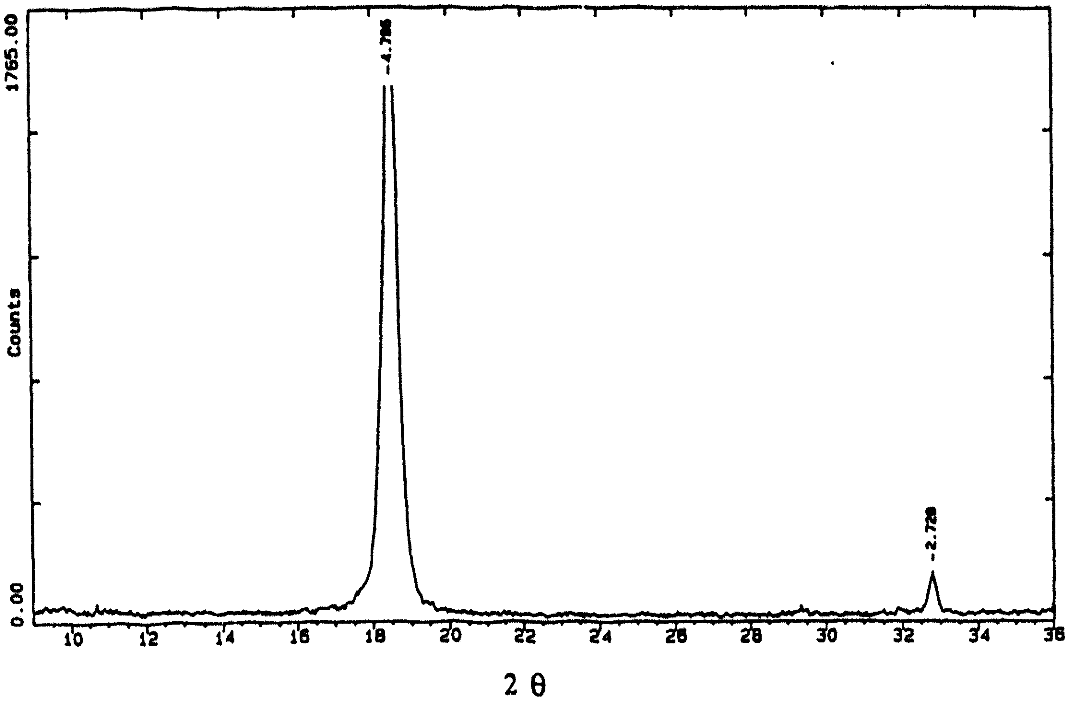


Figure 17. X-ray diffraction of $Mg(OH)_2$

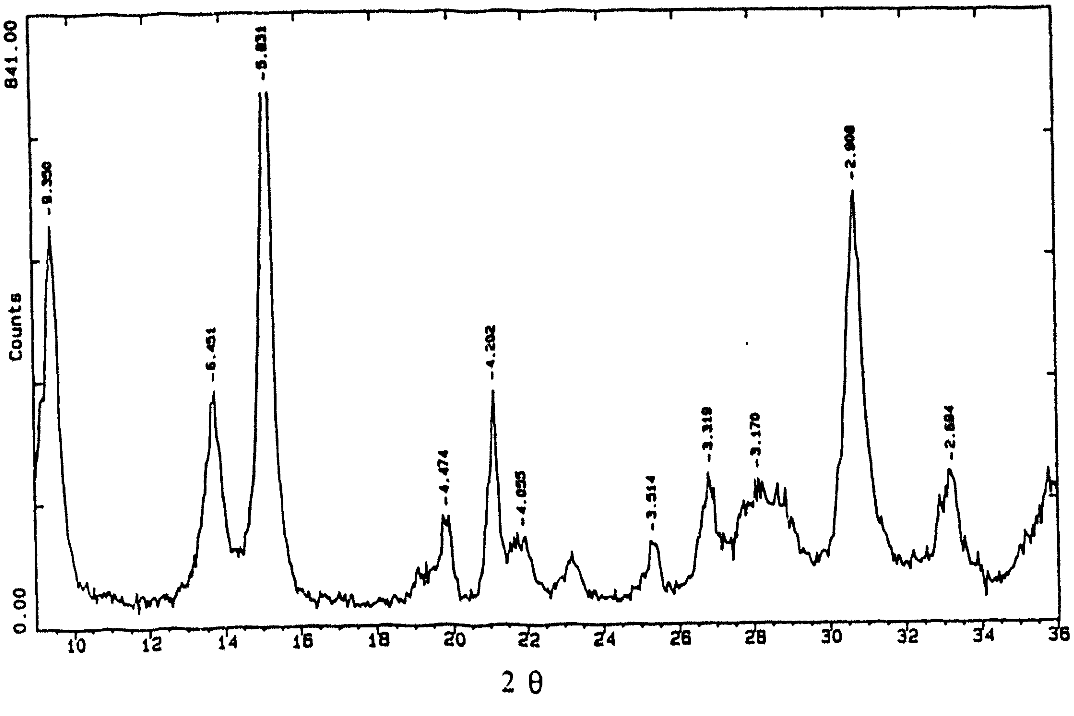


Figure 18. X-ray diffraction of $MgCO_3$

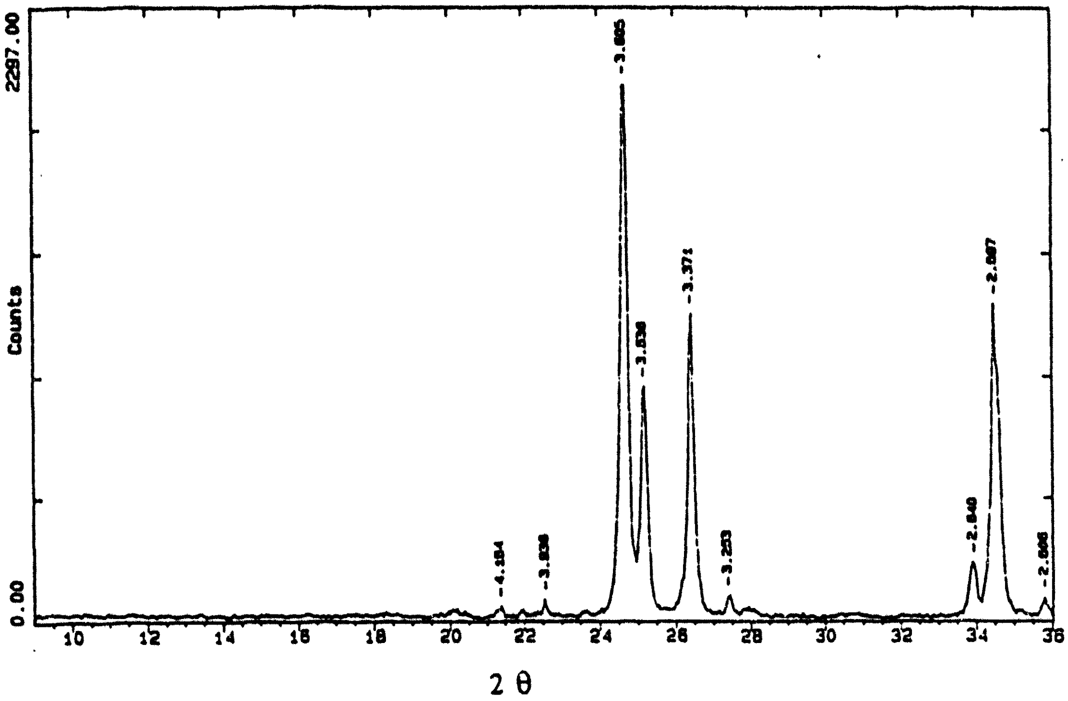


Figure 19. X-ray diffraction of $MgSO_4$

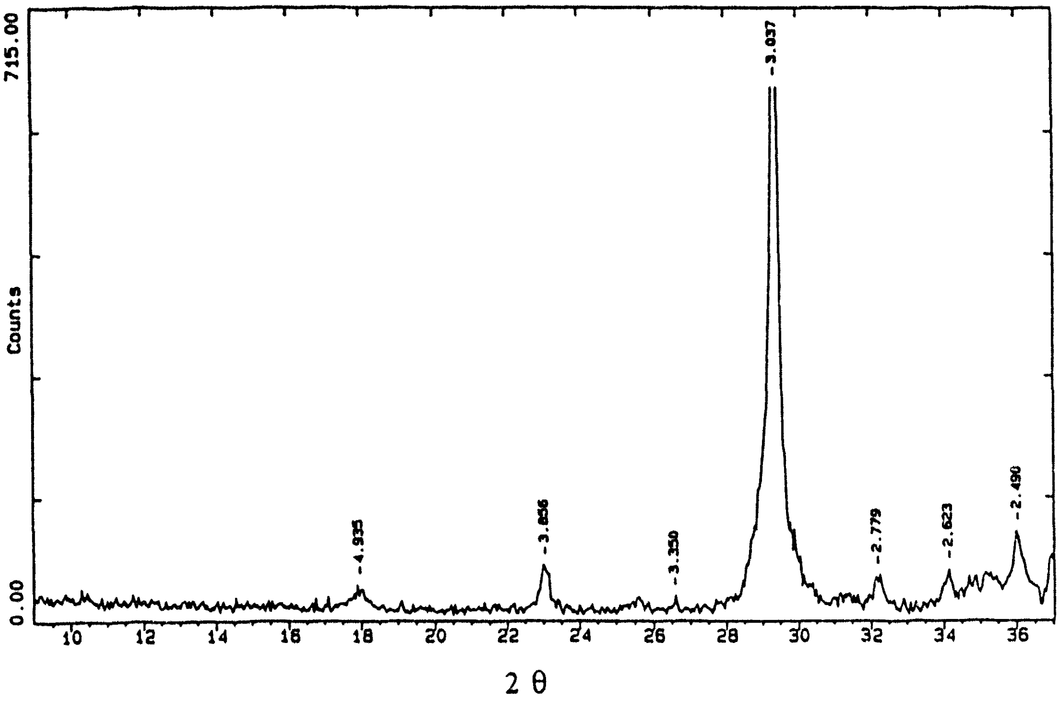


Figure 20. X-ray diffraction of type N dolomitic lime reacted at 1000°F

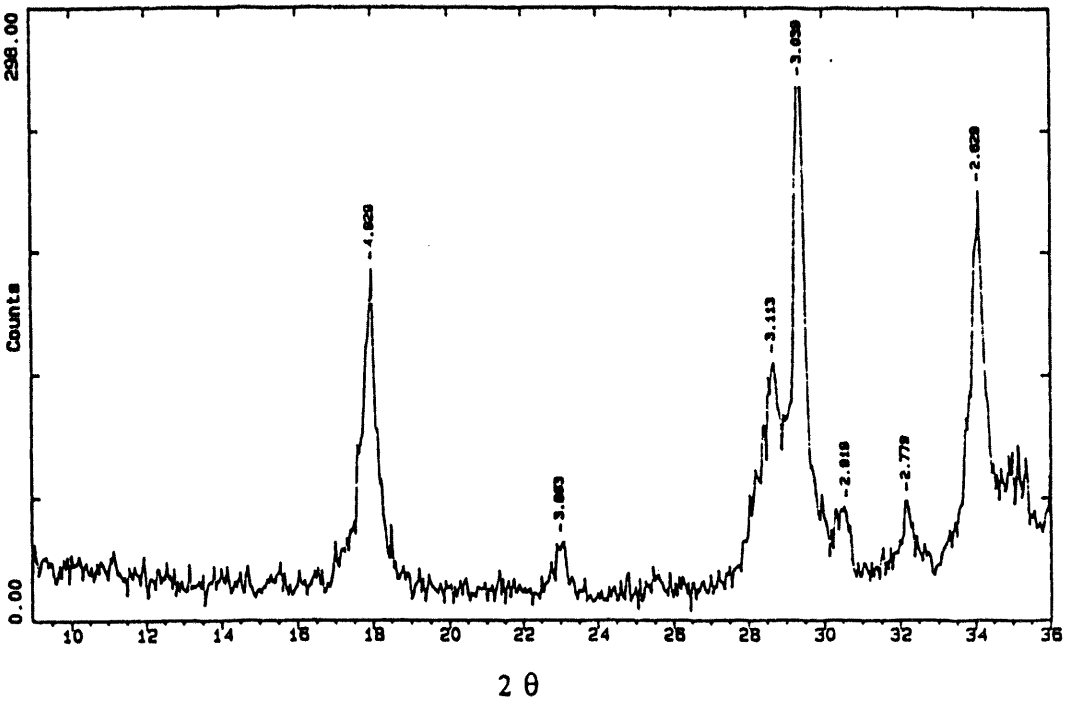


Figure 21. Diffraction of mixture of type N dolomitic lime reacted at different temperatures

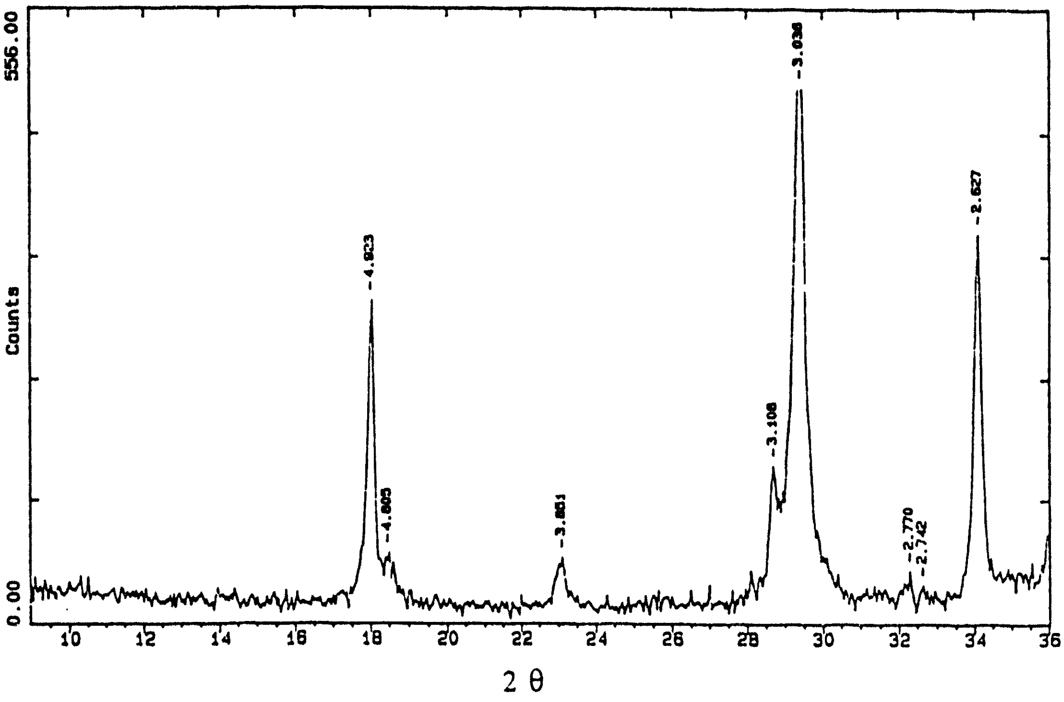


Figure 22. Diffraction of mixture of type S dolomitic lime reacted at different temperatures

There were lots of peaks observed for $MgCO_3$ in this range as shown in Figure 18. The main peaks occurred at 2θ of 9.5, 13.7, 15.2, 21.1 and 30.7. These peaks were easily distinguished from the peaks of previous compounds. Pure $MgSO_4$ also had distinguished peaks as shown in Figure 19. Its main peaks were at 2θ of 24.7, 25.2, 26.3 and 34.4.

As reference to the analysis of the above pure compounds, tentative identification of the products of the sorbent - flue gas reaction was made.

The diffraction pattern of type N dolomitic sorbent sample pre-injected at 1000°F was shown in Figure 20. The peaks that appeared at 2θ of 18.0 and 34.0 for pure type N dolomitic lime, calcium hydroxide and calcium oxide became much lower now. Their peaks at 28.7 could not be detected here. Instead, there was a high peak occurring at 2θ of 29.4, which was only seen in the diffraction of dolomitic lime in Figure 11 as a small peak and could not be matched with any peak in the previous patterns for other pure compounds. No representative peaks for $CaSO_3$, $CaSO_4$+$2H_2O$, $Mg(OH)_2$, $MgCO_3$, or $MgSO_4$ were matched, leaving peaks at 2θ of 23.0, 26.6, 29.4, 32.2 and 36.0 unexplained.

Recall that there might be different crystal structures for the same compound, and these might result in completely different diffraction patterns. The unknown peaks values were checked against diffraction files[12,13]. It was found that the highest peak around d=3.04 was very likely caused by calcium carbonate (calcite syn) which had its 100% peak just at d=3.04. However, the real count in Figure 20 might have been enhanced by another form of calcium carbonate (calcite) which had its three representative peaks at d=3.03, 1.87 and 3.85. The existence of these two kind of $CaCO_3$ helped to explain the peaks at 2θ of 29.4 (d=3.04) and 23.0 (d=3.85), indicating strong tendency of carbonation when type N dolomitic lime was reacted at 1000°F with flue gas constitutes.

In addition, the peak at 2θ of 32.2 was identified as the third representative peak (d=2.78) of a form of calcium oxide (lime syn), which had its other stronger peaks out of the range of this measurement. Thus, the tendency of calcium hydroxide dehydration was evident.

At the curiosity of finding all possible compound diffraction patterns after sorbent - flue gas reaction, products from different drop tube temperatures were mixed for type N and type S dolomitic sorbents. The diffraction pattern for the mixture from type N dolomitic sorbent was shown in Figure 21. Five peaks occurred at the same position as in Figure 20, which were at 2θ of 18.0, 23.0, 29.4 32.2 and 34.2, confirming the formation of calcium carbonate and calcium oxide. It is worth noting that relative count (height) of peaks in Figure 21 did not differ as much as it was in Figure 20. This was likely caused by the mixing of sample, since certain products might alternatively dominate when reactions happened at different temperatures and the mixing effect averaged them out. The relatively high peak at 2θ of 28.7 in Figure 21 was also seen in type N dolomitic lime, calcium hydroxide and calcium oxide, indicating large amount of un-reacted sorbent in some temperatures. The peak at 2θ of 30.6 was not identified yet.

The diffraction pattern for mixture of type S dolomitic sorbent reacted at different temperatures were shown in Figure 22. The pattern here looked quite similar as the one in Figure 21. Peaks at 2θ of 18.0, 28.7 and 34.0 were detected, indicating certain portion of un-reacted sorbent. Again, the highest peak occurred at 2θ of 29.4 and another peak at 23.0, which indicated strong tendency of carbonation to the calcium part of the dolomitic sorbent. In addition, the peak at 2θ of 32.2 showed the tendency of de-hydration. There was one new peak occurred at 2θ of 32.7 (d=2.74), which was identified as one form of magnesium carbonate (magnesite syn). The formation of $MgCO_3$ was very interesting. Since this was not detected in other products, this might indicate that $Mg(OH)_2$ was more reactive to CO_2 than MgO in duct injection or filter collection conditions. This might be an important aspect to note when using type S dolomitic lime as duct injection sorbent.

Unfortunately, no exact form of sulfur existence was successfully identified in the range tested. There was no match when comparing the peaks with all the forms of $CaSO_4$ that might have peaks in the range measured. There was no match with those forms $MgSO_4$ that might have peaks in this range either. Another difficulty came from the fact that there was no diffraction files found for either calcium sulfite or magnesium sulfite. It seemed that more literature should be searched and an extended range of scanning should be used in further work in order to properly determine the related compounds.

F. RE-HYDRATION STUDIES

Recovering available sorbent by re-hydration was the core of this project. Re-hydration processes were conducted in two ways: atmospheric hydration and pressurized Hydration.

Atmospheric hydration was performed in open beakers. The post injected samples were first dispersed in about 10 ml of water in the beakers. Then, excess water was added and the beakers were put on a hot plate. After keeping the slurry boiling for 1 hour, the beakers were removed and put into an oven that was set at 240°F, so that the hydrated samples could be dried. During the hydration process, additional water was used to wash the wall of beakers. Approximately 100 ml water was used in hydrating about 1.5 grams of sample.

Pressurized hydration was conducted in a specially made reaction bomb. The pressure release valve was set at 110 psi for release of overly pressurized gas inside. The valve will shut off effectively when the pressure was reduced to about 80 psi. The samples to be hydrated was first dispersed in about 10 ml of water, then excess water was added to bring the total volume of slurry to about 70 ml. After the bomb was sealed, compressed air was used to bring the pressure inside the unit to 80 psi, at which dolomitic quicklime was usually deeply hydrated in industry. Then, the reaction bomb was heated up in an oil bath (320-380°F, oil temperature), so that the hydration inside the pressurized bomb might happen in a vaporized state. High pressure caused by the vaporization of water was released by the valve. One hour later, the unit was cooled down and the pressure was manually released. Then the hydrated lime slurry was poured into a beaker and dried in the oven as described above.

It is important to note that the final hydrated products from the drying oven were all caked as clumps. This was different form the dried hydrated samples obtained before when using a fixed bed sample preparing system.

The original elemental analyzing results are listed in Table 4 for type N dolomitic lime and Table 5 for type S dolomitic lime, respectively.

Hydrogen, carbon and sulfur contents after hydration were measured after both atmospheric and pressurized hydration processes. As compared to the data before hydration, the extent of hydration, the extent of carbonation with hydration and a sulfur content balance can be obtained. Since sample weight changes in the hydration processes, the weight percentage of H, C and S before and after hydration can not be compared directly. Since the absolute amount of calcium and magnesium would not change in hydration process, CaOMgO was selected as a weight bases for these comparisons. The changes of ratios of H/CaOMgO, C/CaOMgO and S/CaOMgO before and after hydration should be reliable measures on the extent of hydration, carbonation and sulfur balance.

By considering H as in the form of OH^-, C as $CO_3^=$ and S as $SO_3^=$ (since more sulfite than sulfate is formed in medium duct injection temperature range) in the dolomitic samples, the amount of CaOMgO can be easily calculated from the data in Table 4 and Table 5. The percentage of CaOMgO in total sample and the ratios of H, C and S to CaOMgO are listed in Table 6 for type N dolomitic lime and Table 7 for Type S dolomitic lime.

By plotting the H/CaOMgO data for type N dolomitic lime in Figure 23, it is seen that the hydration process significantly increased the hydrogen content in each sample. Pressurized hydration was more effective than atmospheric hydration. In addition, the extent of hydration was affected by the initial extent of dehydration in the primary injection process. All these three curves showed extreme values at 1000°F.

Figure 24 showed the extent of carbonation that happened in accompany with hydration. Usually the hydration process is conducted in a closed system in industry to exclude the influence of atmospheric CO_2, so that a pure, fine and reactive product can be obtained. Our atmospheric hydration reported here was conducted in open air. It is seen that carbonate content increased

Table 4 Analytical data for type N dolomitic samples

Sample preparing conditions		Blank*	Temperature (°F) 800	900	1000	1100	1200
After atmospheric hydration (% by weight)	H	2.82	2.28	2.14	1.25	1.65	1.54
	C	0.85	2.26	2.74	5.59	4.68	4.61
	S	--	2.14	2.06	3.08	2.02	2.87
	TGA	1.53	1.12	1.13	1.06	1.44	1.43
After pressurized hydration (% by weight)	H	2.86	2.45	2.36	1.57	1.72	1.87
	C	0.96	2.12	2.65	5.28	4.33	4.19
	S	--	1.76	1.79	2.61	3.47	1.97
	TGA	1.49	1.11	1.11	1.07	1.42	1.51

Note: * The type N blank sample was not injected into the drop tube reactor, the data listed under "after duct injection" was the analytical results for the original dolomitic lime.

** TGA terms are the weight increase ratio of 1 hour weight to initial weight, not in " %". Time was counted from the moment when reactant gas was switched in.

Table 5 Analytical data for type S dolomitic samples

Sample preparing conditions		Blank*	Temperature (°F)				
			800	900	1000	1100	1200
After atmospheric hydration (% by weight)	H	2.79	2.46	2.16	1.79	1.95	1.63
	C	1.05	1.77	2.84	4.33	4.02	5.33
	S	--	1.81	2.91	3.38	2.03	2.40
	TGA	1.64	1.14	1.11	1.10	1.43	1.59
After pressurized hydration (% by weight)	H	2.67	2.39	2.13	1.70	1.93	1.61
	C	1.40	1.66	2.55	4.19	3.95	5.36
	S	--	2.02	2.98	3.03	1.20	2.12
	TGA	--	1.12	1.13	1.10	1.43	1.60

Note: * The type S blank sample was not injected into the drop tube reactor, the data listed under "after duct injection" was the analytical results for the original dolomitic lime.

** TGA terms are the weight increase ratio of 1 hour weight to initial weight, not in " %". Time was counted from the moment when reactant gas was switched in.

Table 6 Hydration effects for type N dolomitic lime

Sample preparing conditions		Blank	Temperature (°F)				
			800	900	1000	1100	1200
After duct injection before hydration (% by weight)	CaOMgO	79.19	74.40	73.31	69.37	70.09	71.7
	H/CaOMgO	2.55	1.91	1.66	0.23	0.64	0.96
	C/CaOMgO	0.90	2.51	3.91	8.25	6.85	6.63
	S/CaOMgO	0.00	4.01	3.56	5.93	5.92	3.27
After atmospheric hydration (% by weight)	CaOMgO	71.49	66.96	66.58	62.05	63.99	63.5
	H/CaOMgO	3.95	3.40	3.21	2.02	2.57	2.43
	% increment	54.7	78.1	93.3	791.4	304.0	153.
	C/CaOMgO	1.19	3.38	4.11	9.01	7.31	7.25
	% increment	31.27	34.22	5.22	9.21	6.75	9.48
	S/CaOMgO	0.00	3.19	3.09	4.97	3.16	4.52
	% increment	--	- 20.4	- 13.1	- 16.2	- 46.5	38.0
After pressurized hydration (% by weight)	CaOMgO	70.73	66.43	65.50	61.33	61.64	63.9
	H/CaOMgO	4.05	3.73	3.60	2.56	2.80	2.93
	% increment	58.6	95.4	116.6	1029.	339.5	205.
	C/CaOMgO	1.36	3.18	4.04	8.60	7.03	6.55
	% increment	50.07	26.60	3.41	4.20	2.61	-1.10
	S/CaOMgO	0.00	2.65	2.73	4.26	5.64	3.09
	% increment	--	- 33.9	- 23.4	- 28.2	- 4.73	-5.63

Note: * CaOMgO terms are the equivalent CaOMgO percentages in total samples

** % increments are based on the initial content of the element before hydration

Table 7 Hydration effects for type S dolomitic lime

Sample preparing conditions			Temperature (°F)				
		Blank	800	900	1000	1100	1200
After duct injection before hydration (% by weight)	CaOMgO	71.25	69.07	67.65	66.68	67.88	67.5
	H/CaOMgO	4.05	3.33	2.49	1.48	2.13	0.91
	C/CaOMgO	1.07	2.22	3.90	6.70	5.85	8.43
	S/CaOMgO	0.00	3.34	5.57	6.05	3.35	4.56
After atmospheric hydration (% by weight)	CaOMgO	71.01	67.74	64.30	61.29	63.66	61.0
	H/CaOMgO	3.93	3.63	3.36	2.92	3.06	2.67
	% increment	- 2.83	9.00	35.20	97.59	43.87	192.
	C/CaOMgO	1.48	2.62	4.42	7.06	6.31	8.73
	% increment	38.29	18.08	13.42	5.37	7.92	3.54
	S/CaOMgO	0.00	2.67	4.52	5.51	3.18	3.93
	% increment	--	- 20.1	- 19.0	- 8.95	- 5.13	-14.0
After pressurized hydration (% by weight)	CaOMgO	70.85	68.32	65.53	63.27	64.19	61.6
	H/CaOMgO	3.76	3.50	3.25	2.69	3.00	2.62
	% increment	- 6.97	5.13	30.72	82.29	40.78	186.
	C/CaOMgO	1.98	2.43	3.88	6.62	6.16	8.70
	% increment	84.67	9.74	- 0.33	- 1.28	5.33	3.22
	S/CaOMgO	0.00	2.96	4.55	4.78	3.11	3.45
	% increment	--	- 11.4	- 18.4	- 20.9	- 7.26	-24.4

Note: * CaOMgO terms are the equivalent CaOMgO percentages in total samples

** % increments are based on the initial content of the element before hydration

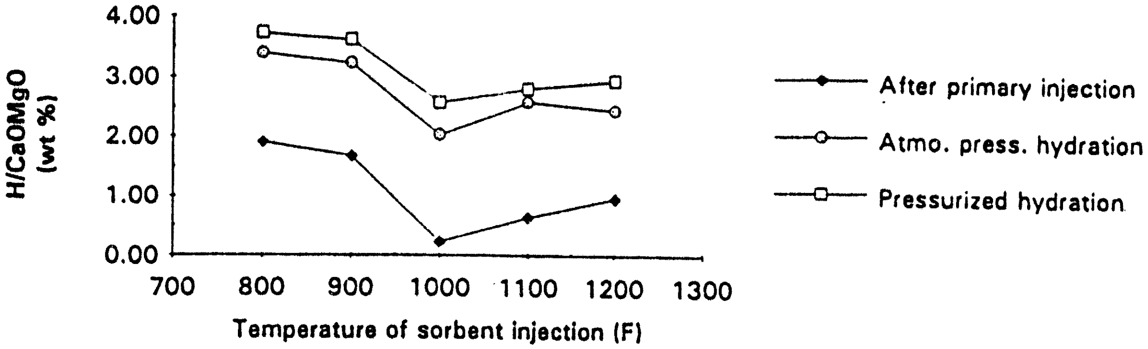


Figure 23. Hydrogen content change for type N dolomitic sorbent

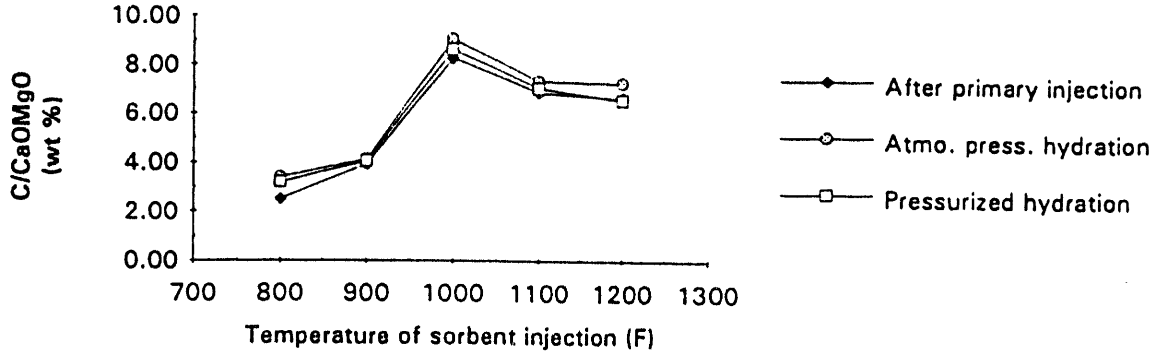


Figure 24. Carbon content change for type N dolomitic sorbent

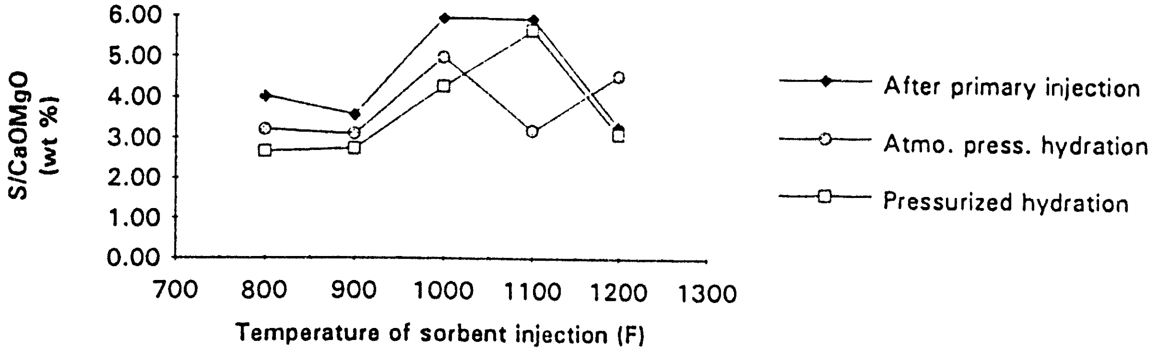


Figure 25. Sulfur content change for type N dolomitic sorbent

after hydration. Air was also not expelled from the pressurized hydration. However, since the hydration mainly happened in a sealed reaction bomb, the carbon content increase for pressurized hydration was a little less than that for the atmospheric hydration.

No clear pattern of sulfur content change was observed on Figure 25 for type N dolomitic lime. In fact, sulfur content should not change in any hydration process. However, it seemed that the sulfur content generally decreased in the hydration processes. It is supposed that this was caused by the errors in analyzing the total sulfur content. Certain portion of sulfite might have been converted into sulfates in the presence of O_2 in the hydration processes. Since $CaSO_4$ decomposes at a high temperature, the measurement of total sulfur depends on the temperature that the furnace on total sulfur analyzer may reach and the decomposition rate of sulfate at that temperature. If certain portion of sulfur was not captured by the analyzer, cases such as Figure 25 would be easily resulted.

For type S dolomitic lime in Figure 26, the extent of hydration was also significant except for the sample primarily prepared at 800°F. Atmospheric hydration seemed to be slightly effective than pressurized hydration.

The extent of carbonation in the hydration process for type S dolomitic lime showed a similar pattern in Figure 27 as for type N dolomitic lime in Figure 24. The atmospheric hydration resulted in higher carbon content than the pressurized hydration. Since the carbonation process has adverse effects on the purity, surface area and reactivity of the hydrated product, carbonation in hydration should be avoided.

There was also a sulfur content decrease observed for type S dolomitic lime after hydration in Figure 28. The same reason is assumed as for type N dolomitic lime. Analytical check for the total sulfur analyzer will be performed during next quarterly work.

There was some concern before these tests on the possibility of hydrating the oxides left over in the central core of spent sorbent after a dense product shell had been formed which made

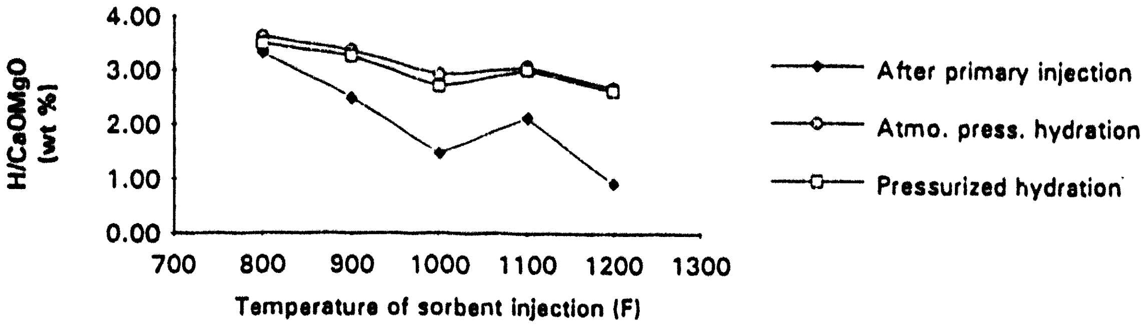


Figure 26. Hydrogen content change in type S dolomitic sorbent

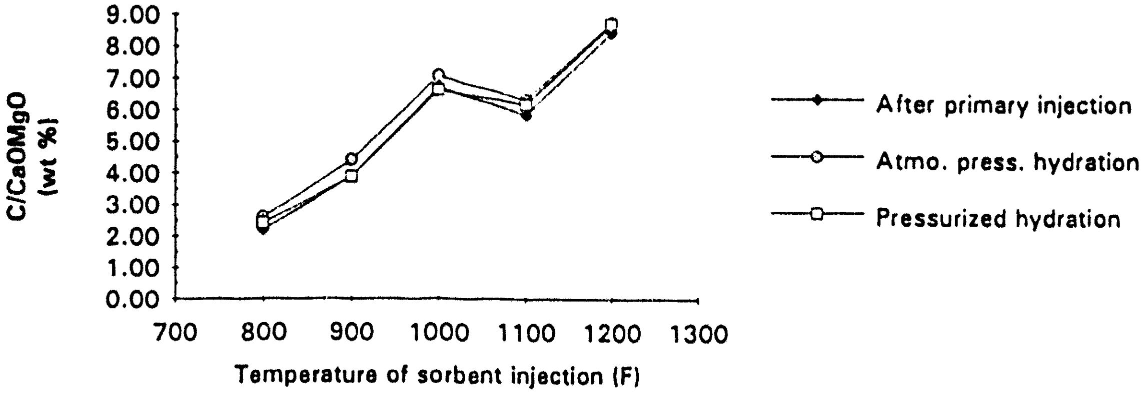


Figure 27. Carbon content change in type S dolomitic sorbent

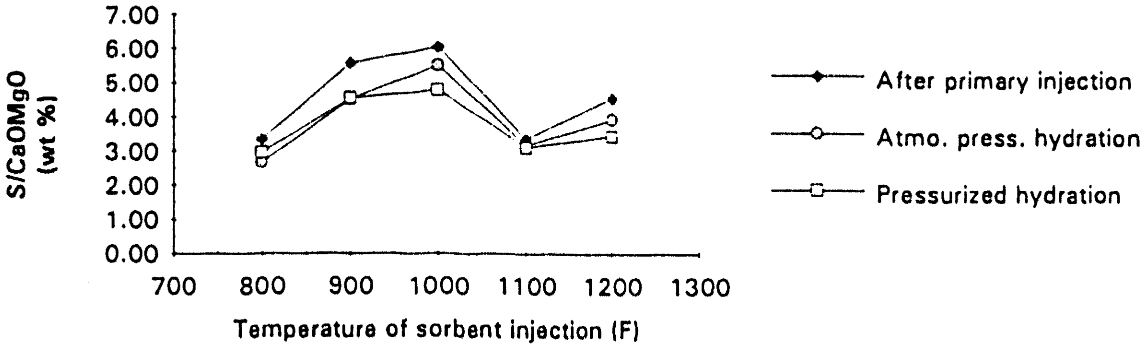


Figure 28. Sulfur content change in type S dolomitic sorbent

it difficult for SO_2 to diffuse through. Recalling that it is expected that the expansion of molar volumes in forming hydroxides will cause the fracture of used sorbent particles to expose fresh and reactive sorbent inside, successful hydration of these oxides is the key step in recovering available sorbent. Tests performed above has proved this possibility.

In order to show the effect of hydration clearly, Figure 29 and Figure 30 were drawn, in which the equivalent amount of H_2O combined in type S dolomitic lime ($Ca(OH)_2Mg(OH)_2$) was taken as the upper water content limit and the amount of water combined on the oxides in each step of operation was compared to it. The original H_2O content line in Figure 29 indicated the equivalent H_2O content in type N dolomitic lime ($Ca(OH)_2MgO$). It is easily seen that large amount of oxides was hydrated, including large portion of MgO.

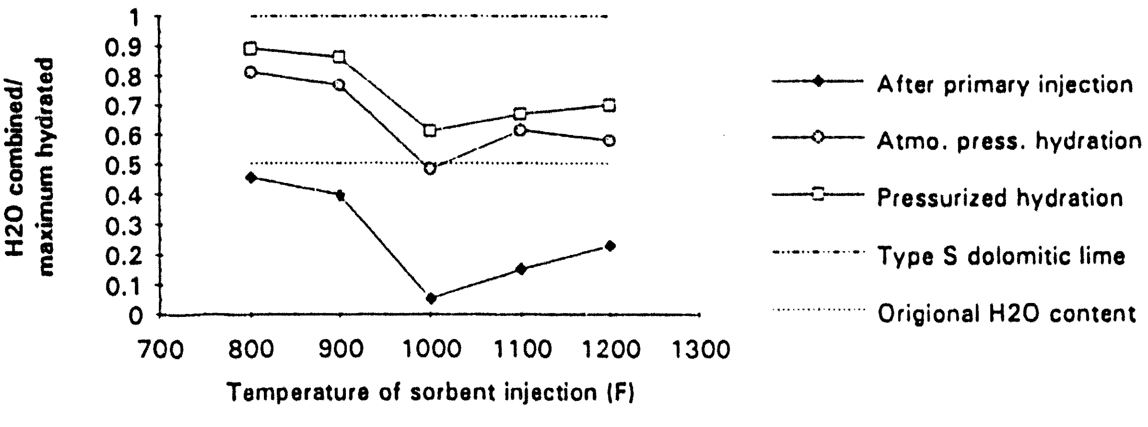


Figure 29. Effect of hydration for type N dolomitic sorbent

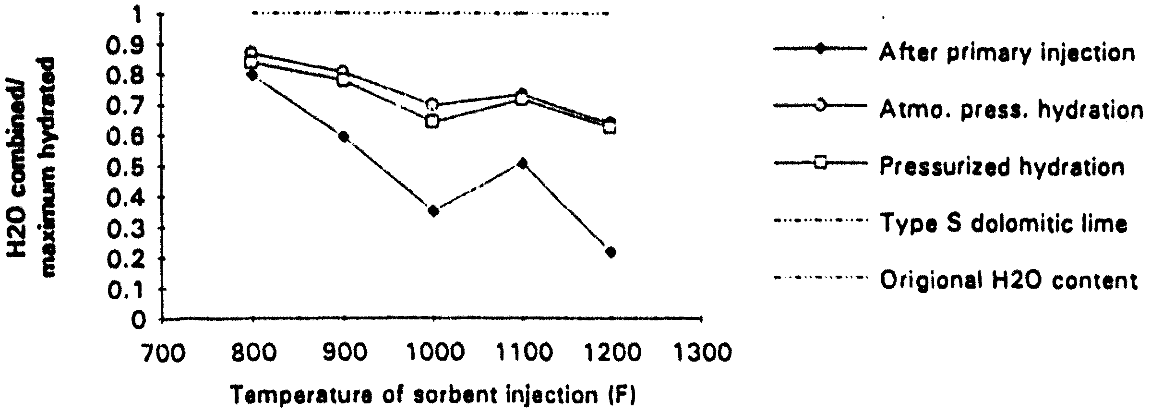


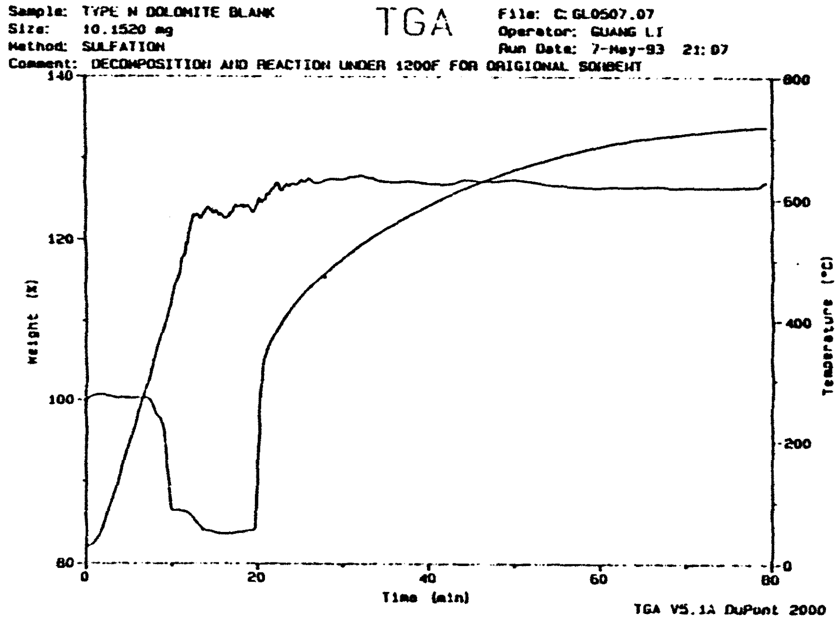
Figure 30. Effect of hydration for type S dolomitic sorbent

G. TGA TESTS ON REACTIVITY

TGA tests were performed to examine the reactivity change after hydration. The weight change 1 hour after the start of the reactions between sorbent and the simulated flue gas reactants was of main concern, even though TGA curves might provide information such as initial reaction rates etc.. Because of the clumping of hydrated particles, these samples were manually crushed and screened with #400 sieve (38 micron opening) before TGA tests.

All TGA tests started from room temperature. Pure nitrogen was first passed through the TGA. A fast ramp was set at 50°C (90°F)/min.. Then an isothermal state was kept when the temperature of the TGA sample reached the temperature at which it was primarily prepared in the drop tube reactor.

The TGA test results were shown in Figure 31 through Figure 42 for type N and type S dolomitic lime injected at different conditions. All TGA curves showed certain extent of weight



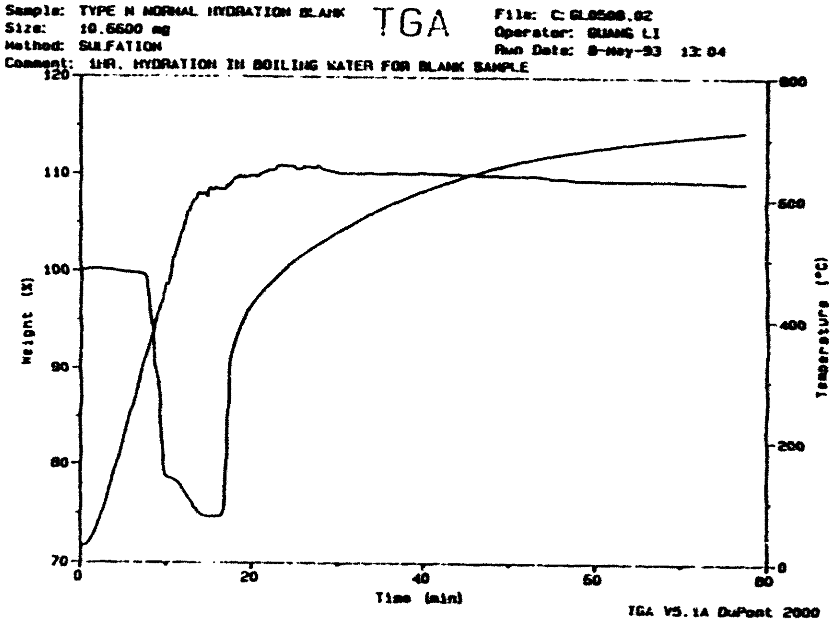
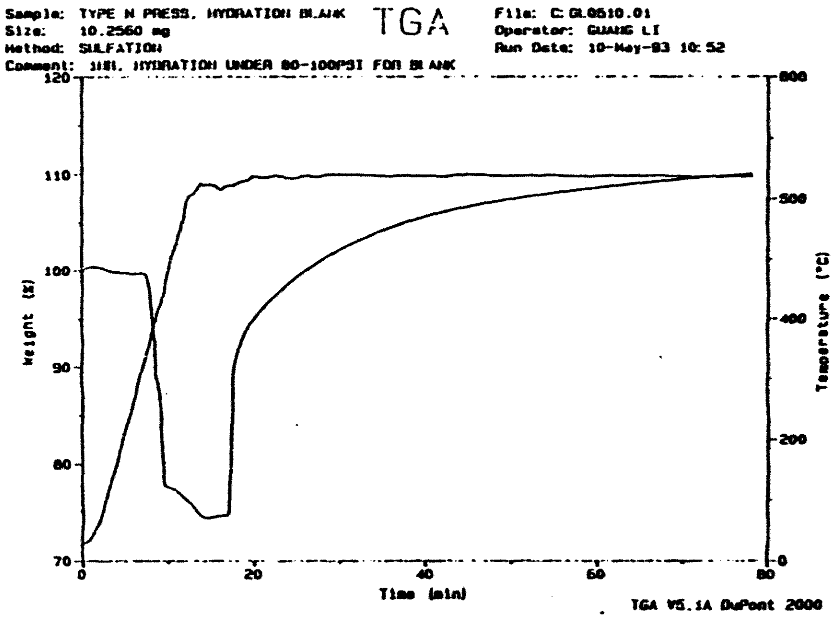
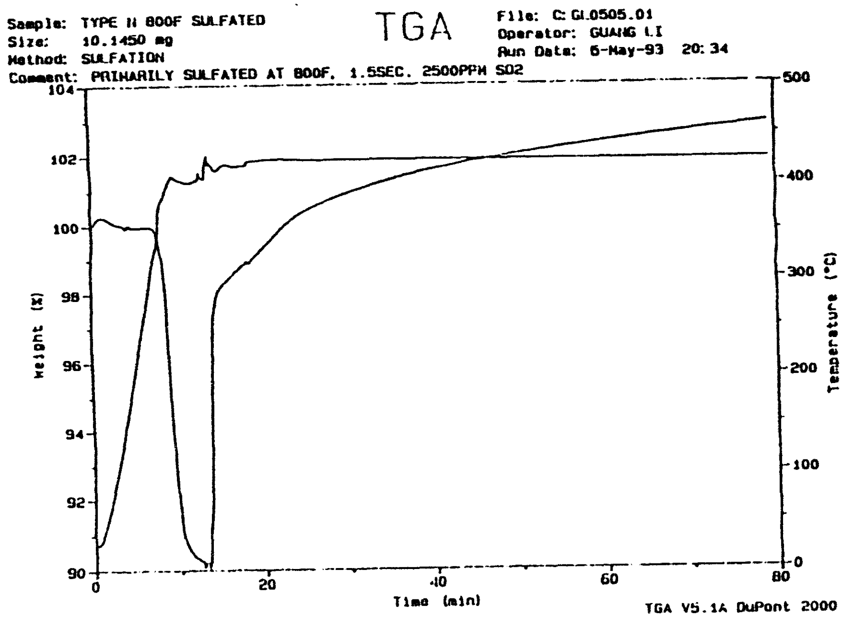
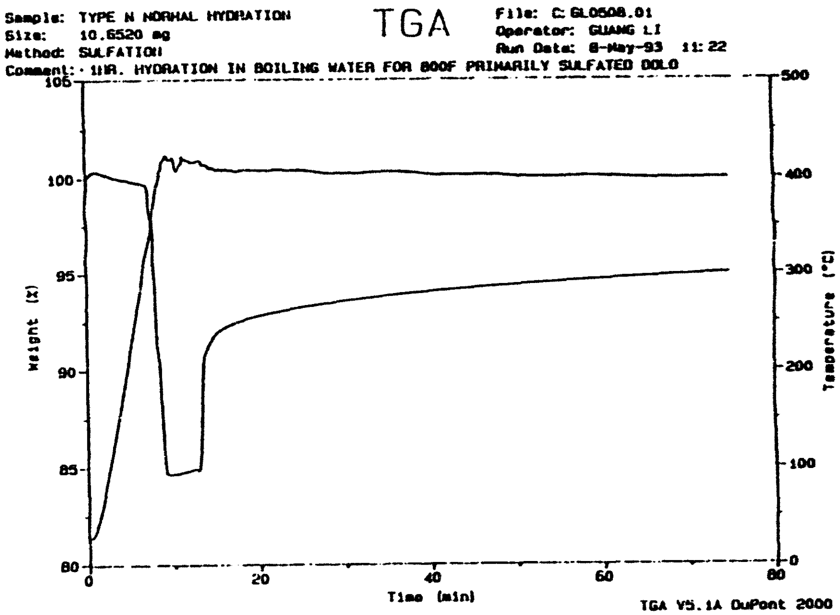


Figure 31. TGA tests for type N dolomitic lime blank

Top:	reactivity of blank
Top Right:	after atmospheric hydration
Right:	after pressurized hydration







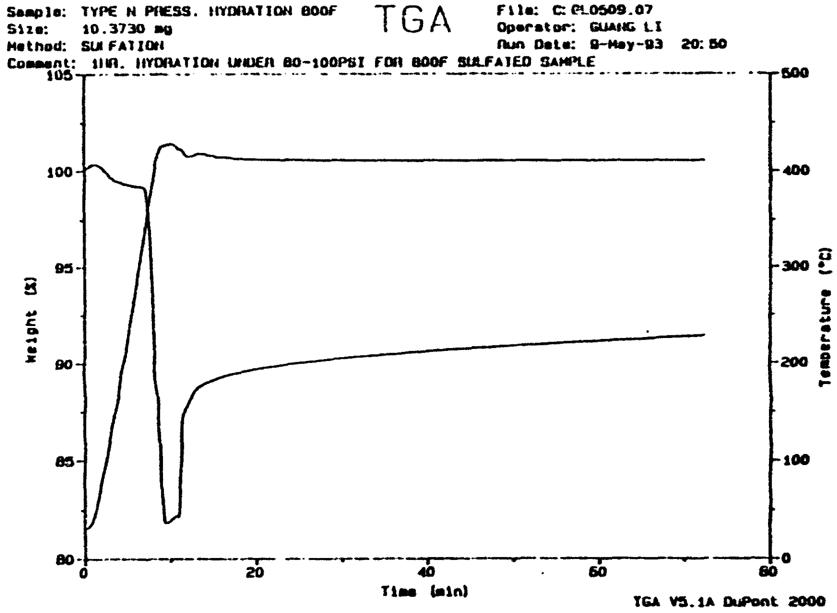
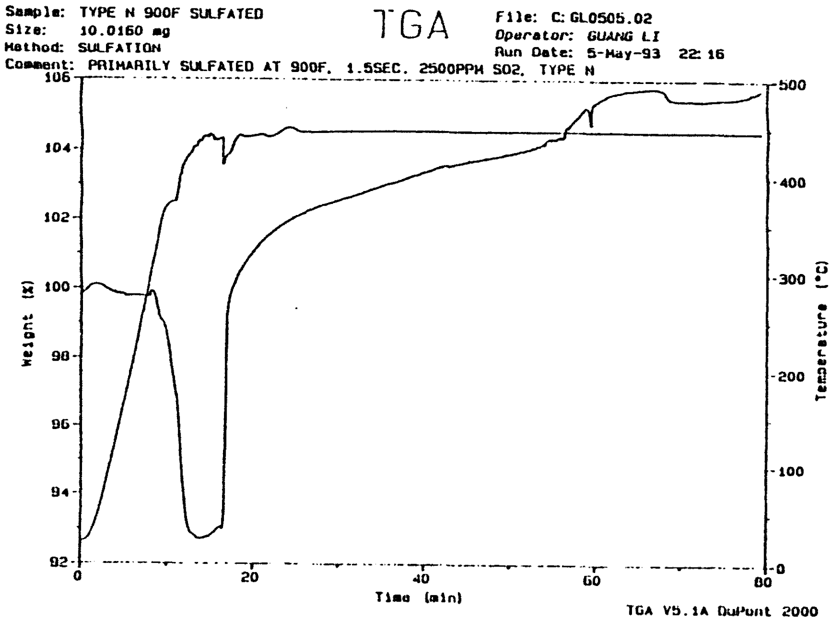
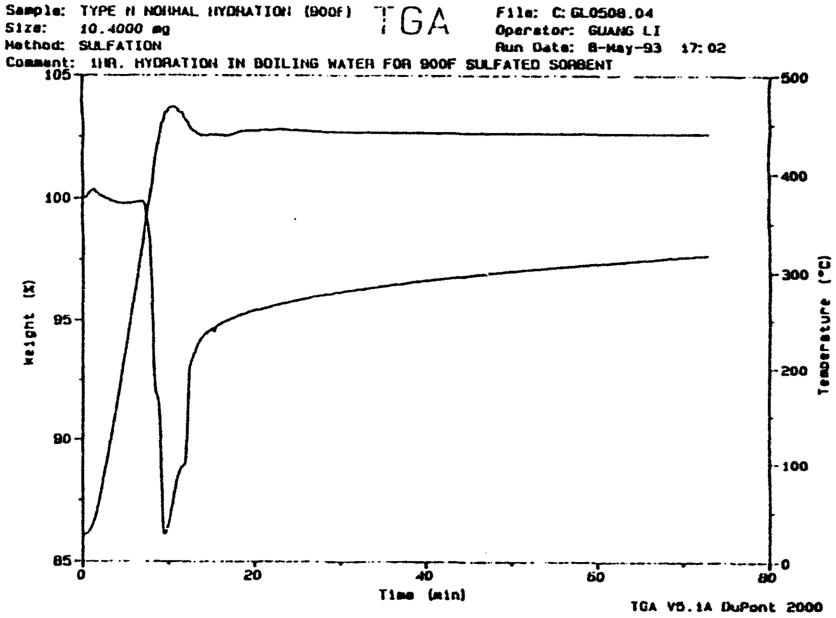


Figure 32. TGA for type N samples pre-injected at 800°F

Top:	after primary injection
Top Right:	after atmospheric hydration
Right:	after pressurized hydration





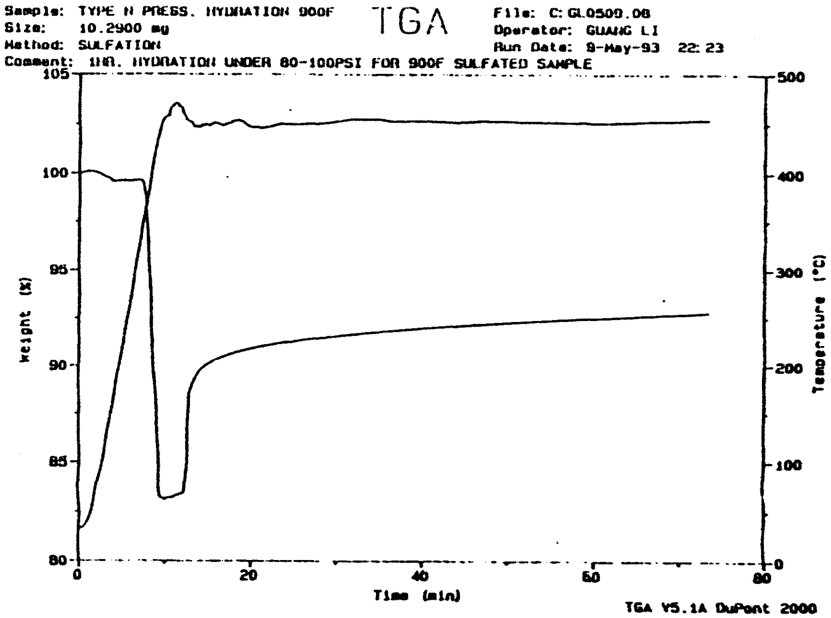
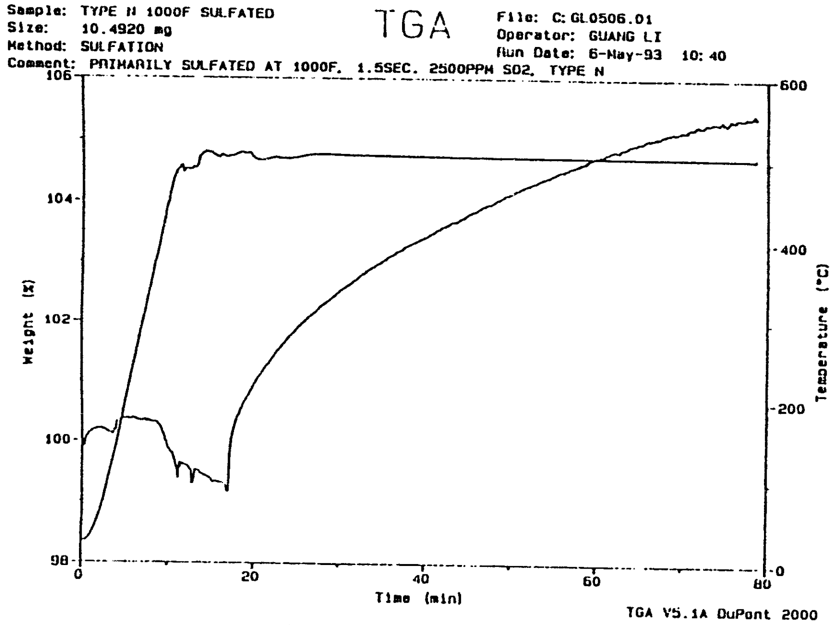


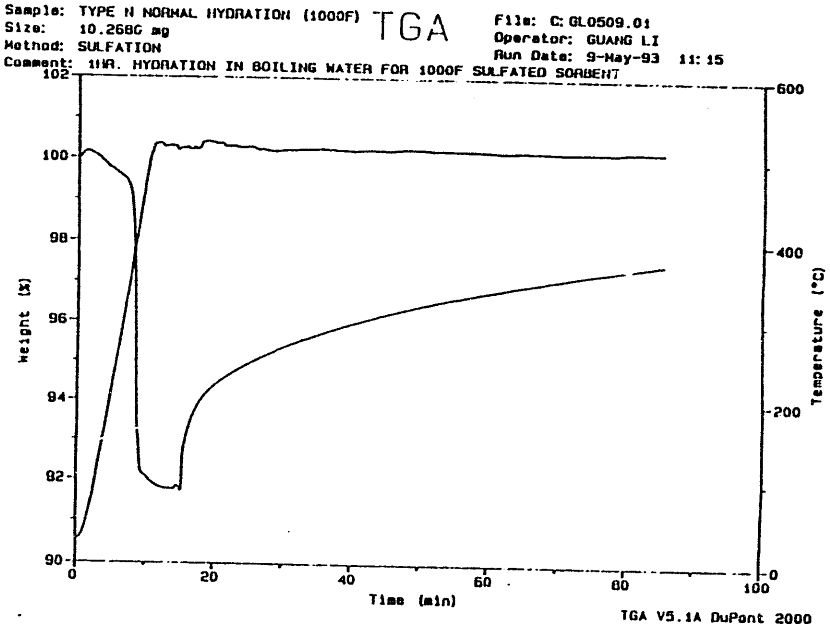
Figure 33. TGA for type N samples pre-injected at 900°F

Top: after primary injection

Top Right: after atmospheric hydration

Right: after pressurized hydration





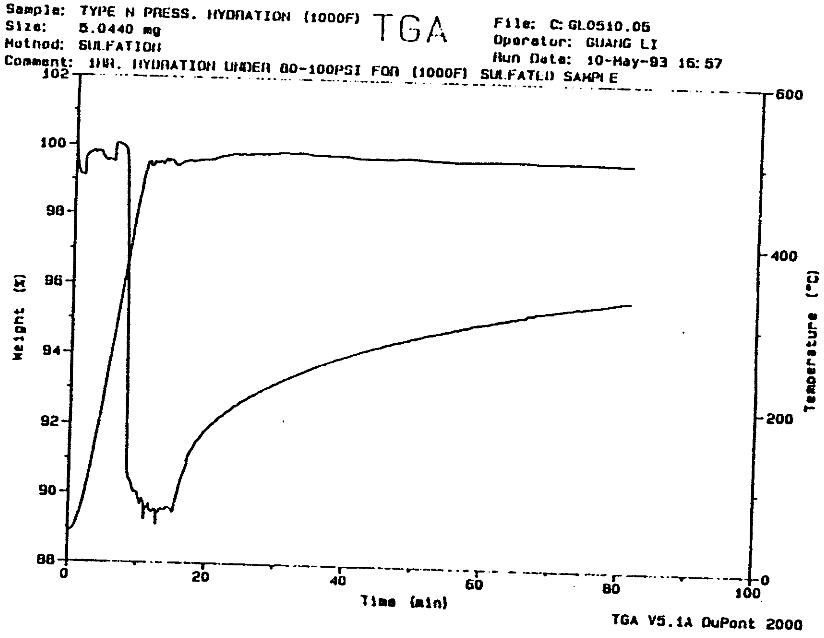
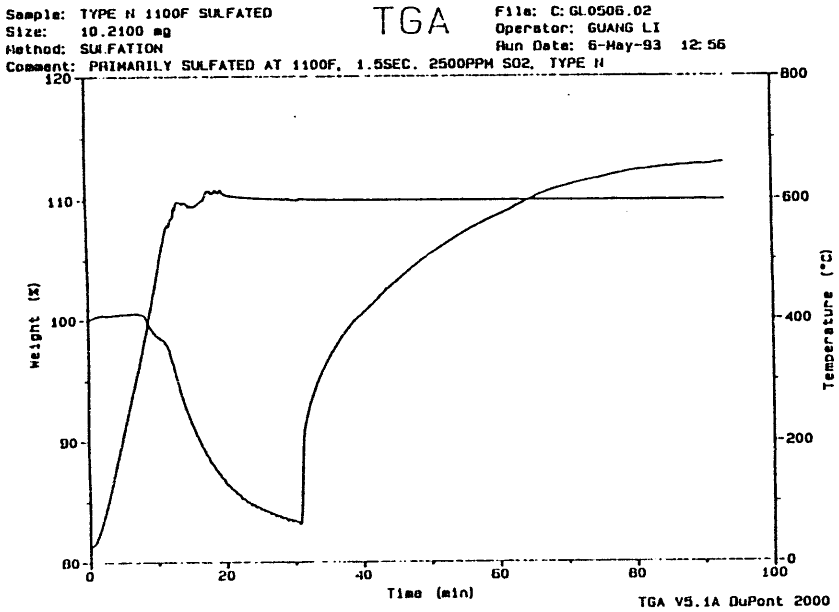
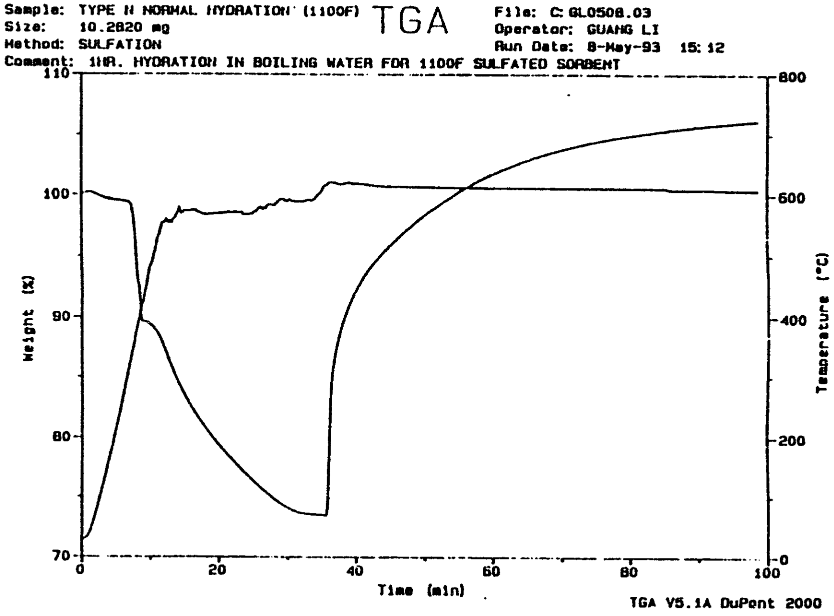


Figure 34. TGA for type N samples pre-injected at 1000°F

Top:	after primary injection
Top Right:	after atmospheric hydration
Right:	after pressurized hydration





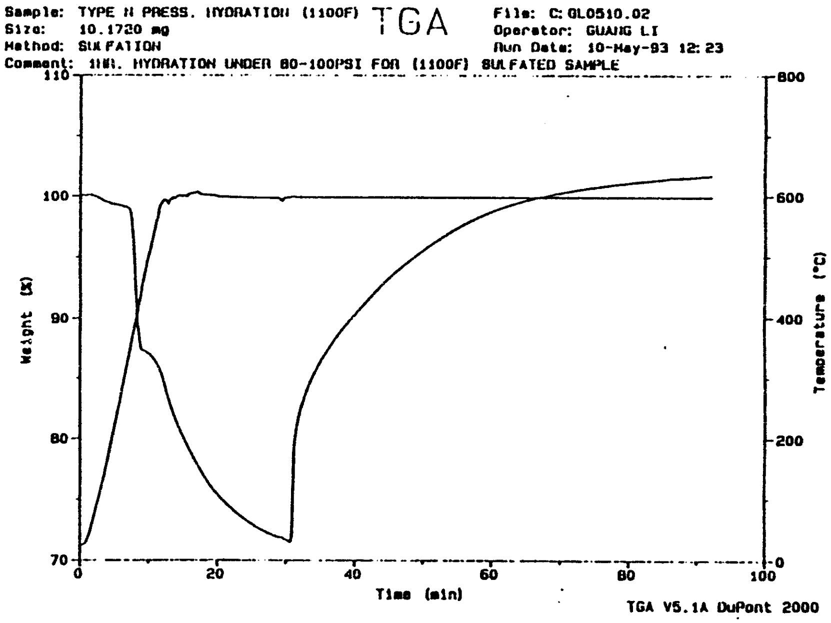
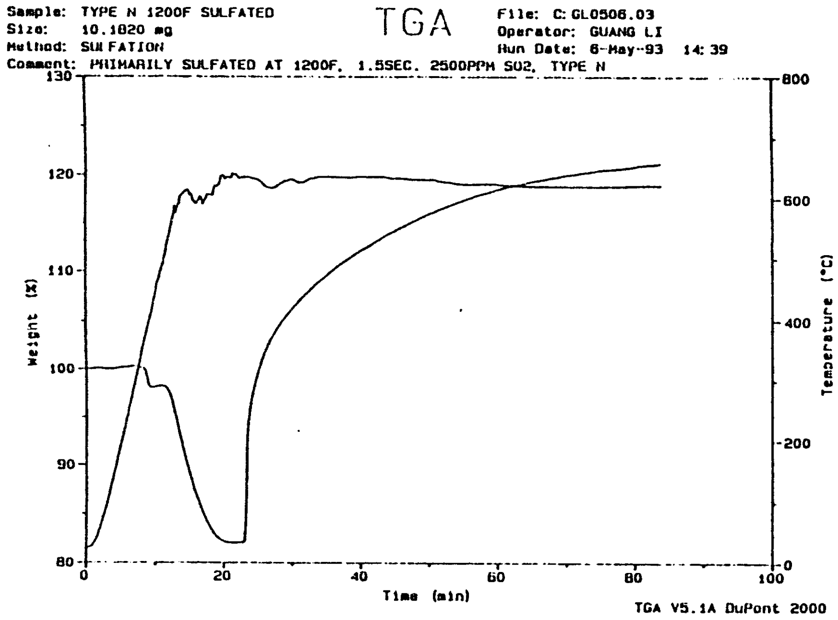
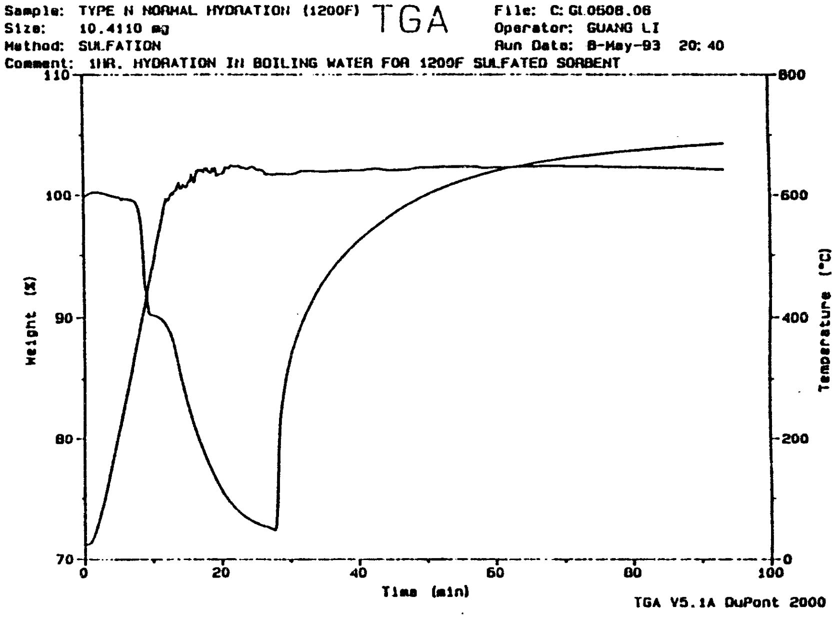


Figure 35. TGA for type N samples pre-injected at 1100°F

Top:	after primary injection
Top Right:	after atmospheric hydration
Right:	after pressurized hydration





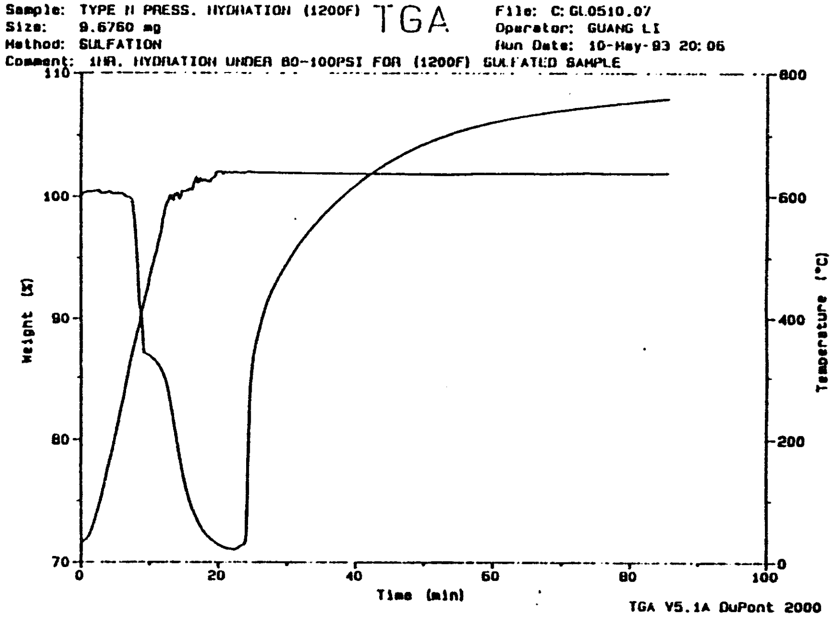
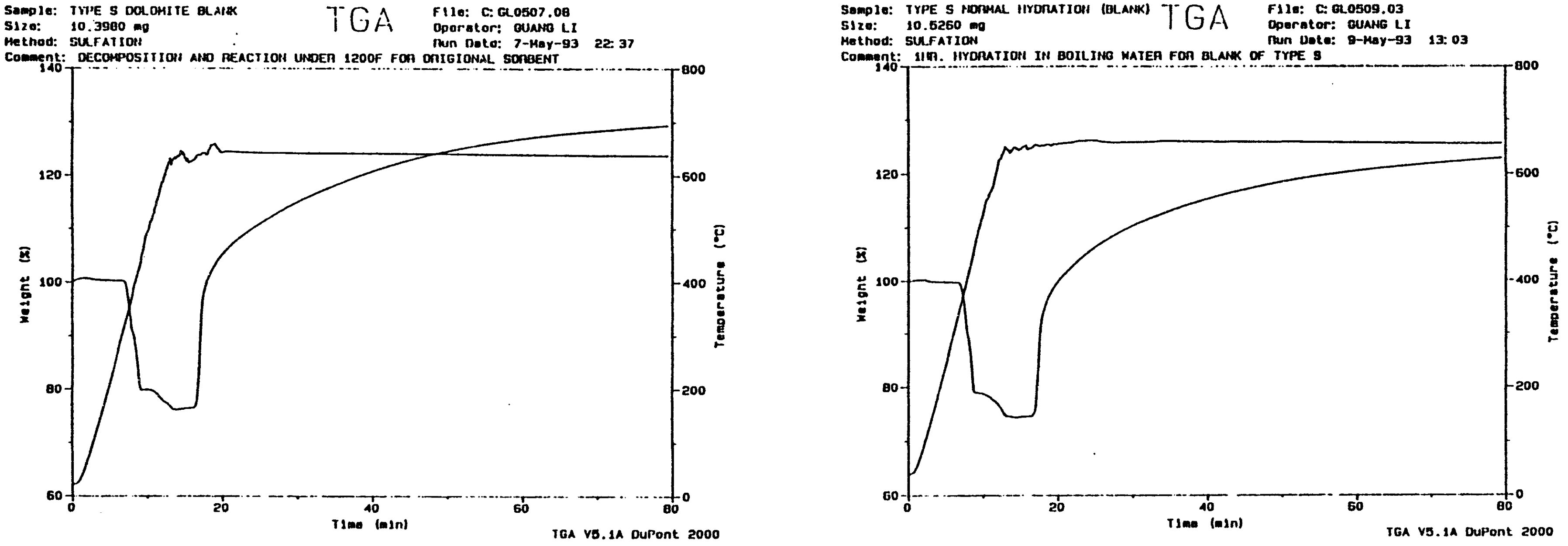


Figure 36. TGA for type N samples pre-injected at 1200°F

Top:	after primary injection
Top Right:	after atmospheric hydration
Right:	after pressurized hydration



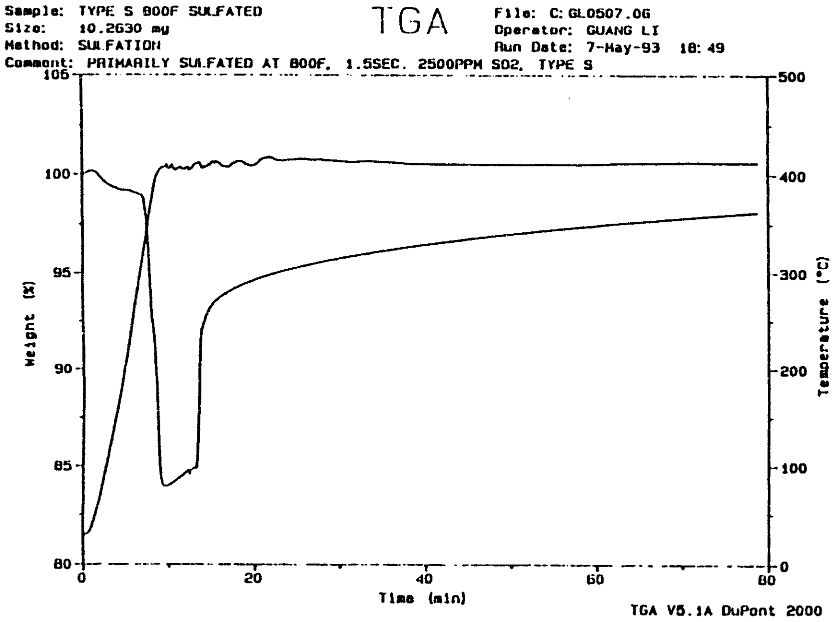
Sample: TYPE S DOLOMITE BLANK
Size: 10.3980 mg
Method: SULFATION
Comment: DECOMPOSITION AND REACTION UNDER 1200F FOR ORIGIONAL SORBENT
File: C:GL0507.08
Operator: GUANG LI
Run Date: 7-May-93 22:37

Sample: TYPE S NORMAL HYDRATION (BLANK)
Size: 10.5260 mg
Method: SULFATION
Comment: 1HR. HYDRATION IN BOILING WATER FOR BLANK OF TYPE S
File: C:GL0509.03
Operator: GUANG LI
Run Date: 9-May-93 13:03

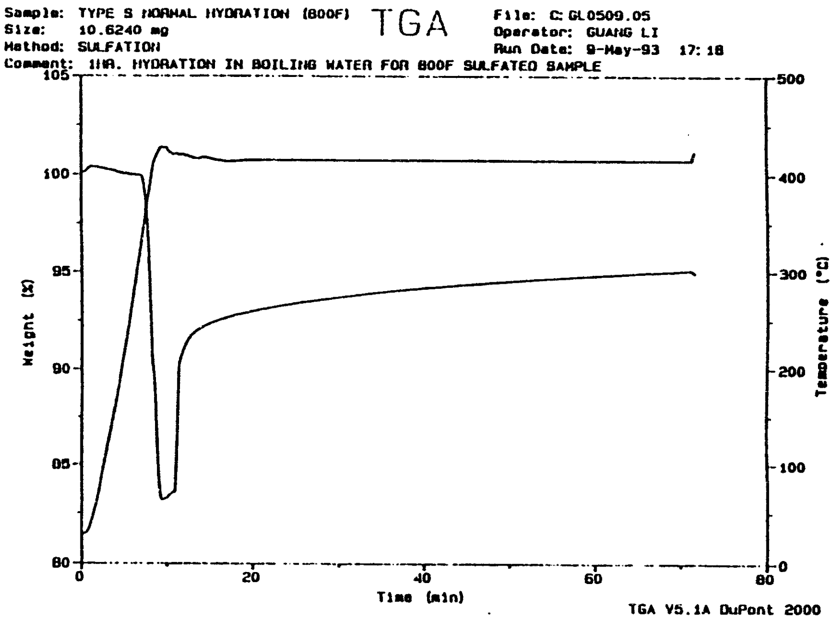
Figure 37. TGA tests for type S dolomitic lime blank

Top: reactivity of blank

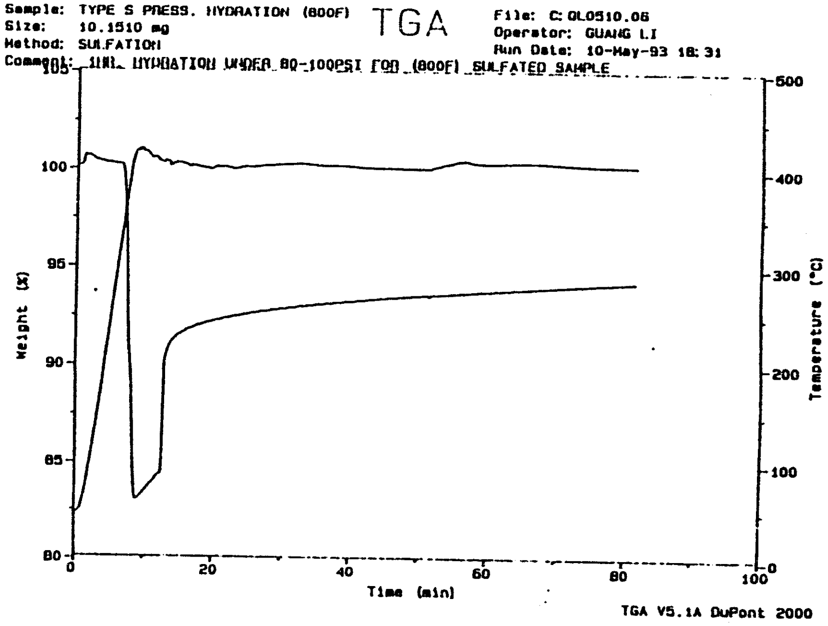
Top Right: after atmospheric hydration



Sample: TYPE S 800F SULFATED
Size: 10.2630 mg
Method: SULFATION
Comment: PRIMARILY SULFATED AT 800F, 1.5SEC, 2500PPM SO2, TYPE S
File: C:GL0507.06
Operator: GUANG LI
Run Date: 7-May-93 18:49



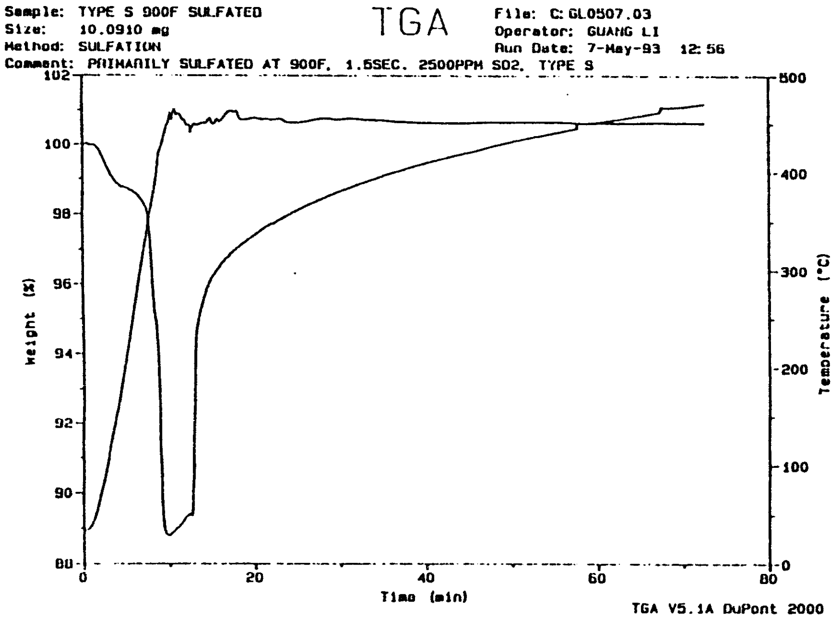
Sample: TYPE S NORMAL HYDRATION (800F)
Size: 10.6240 mg
Method: SULFATION
Comment: 1HR. HYDRATION IN BOILING WATER FOR 800F SULFATED SAMPLE
File: C:GL0509.05
Operator: GUANG LI
Run Date: 9-May-93 17:18

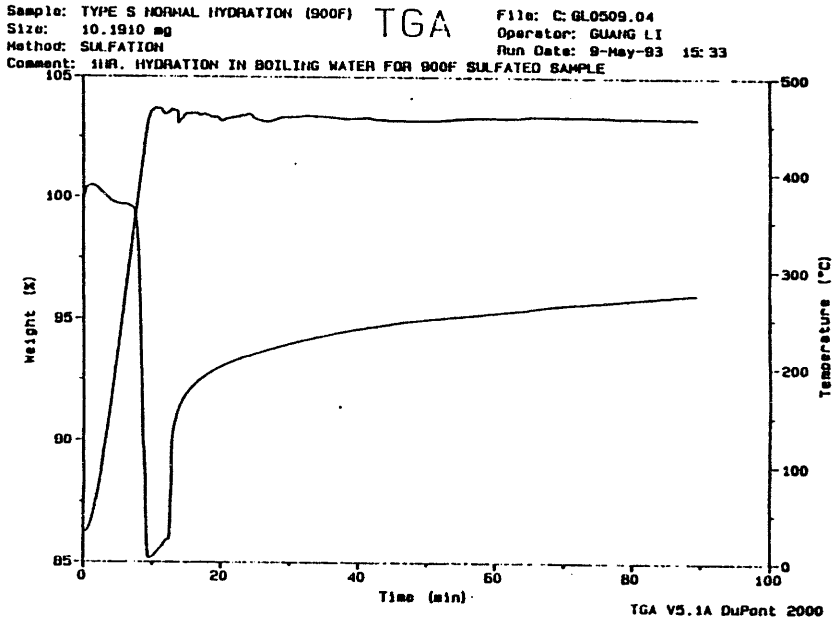


Sample: TYPE S PRESS. HYDRATION (800F)
Size: 10.1510 mg
Method: SULFATION
Comment: 1HR. HYDRATION UNDER 80-100PSI FOR (800F) SULFATED SAMPLE
File: C:GL0510.06
Operator: GUANG LI
Run Date: 10-May-93 18:31

Figure 38. TGA for type S samples pre-injected at 800°F

Top:	after primary injection
Top Right:	after atmospheric hydration
Right:	after pressurized hydration





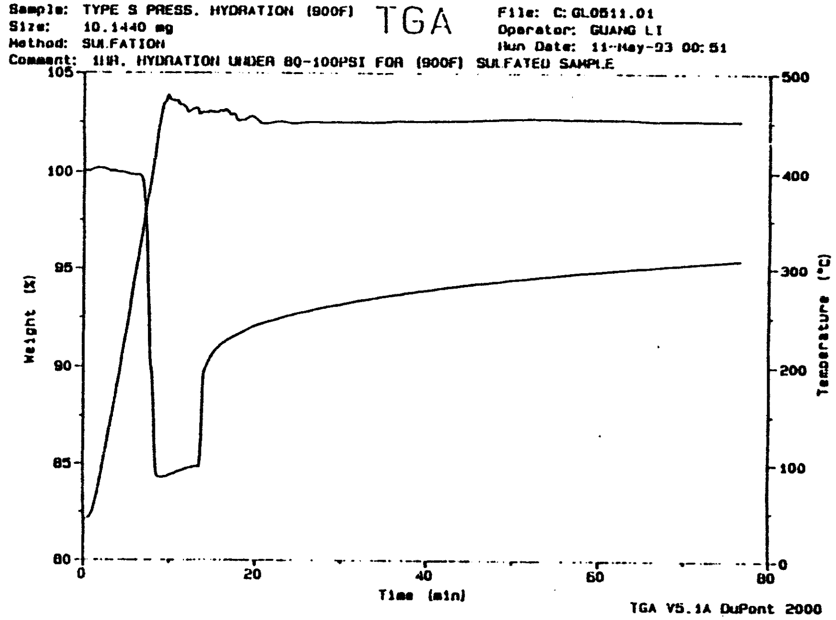
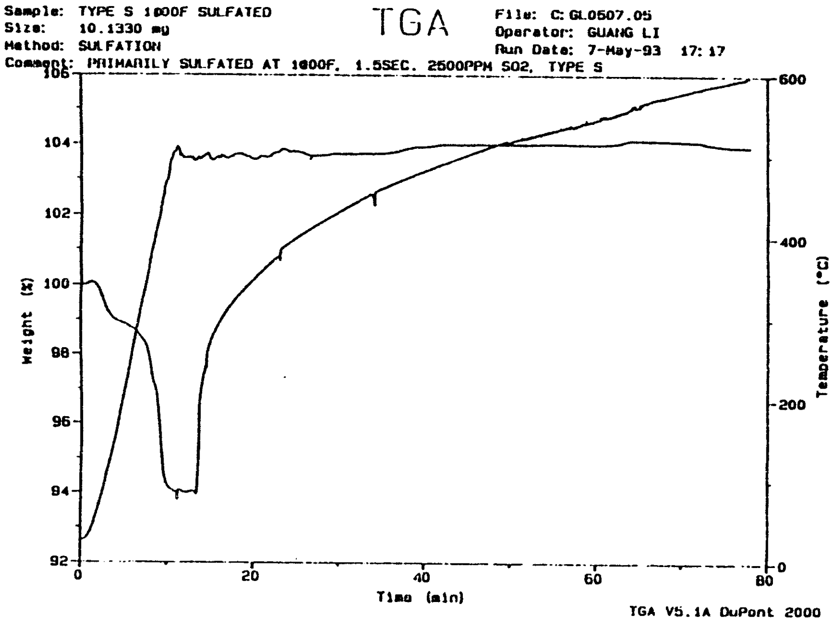


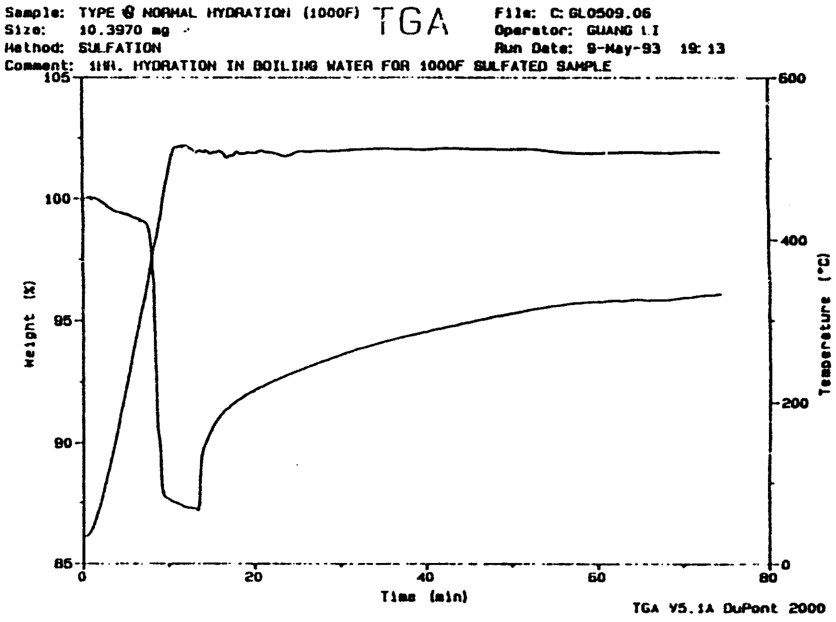
Figure 39. TGA for type S samples pre-injected at 900°F

Top: after primary injection

Top Right: after atmospheric hydration

Right: after pressurized hydration





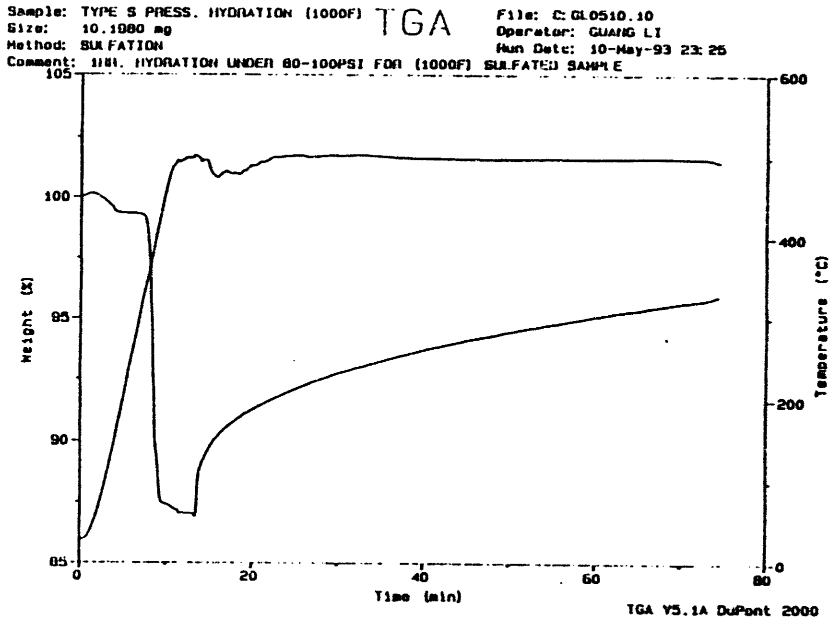
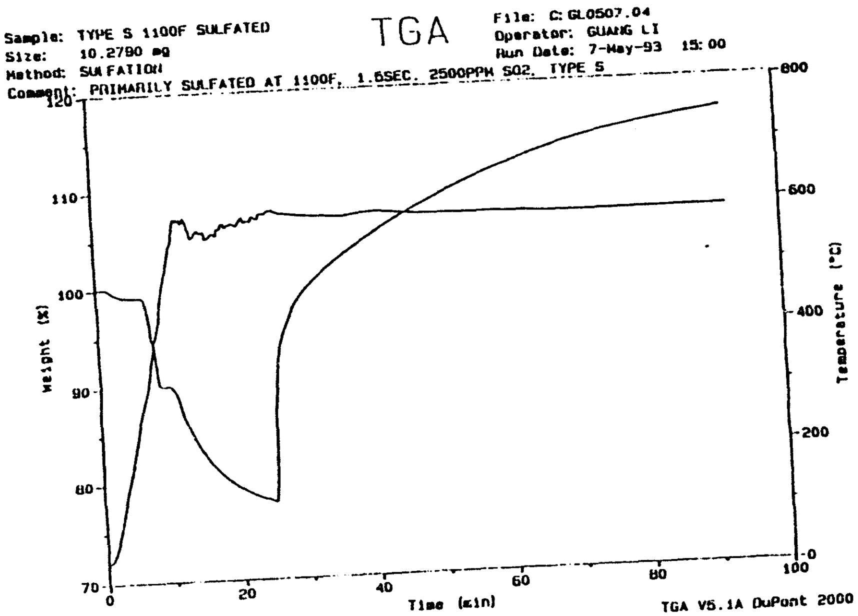


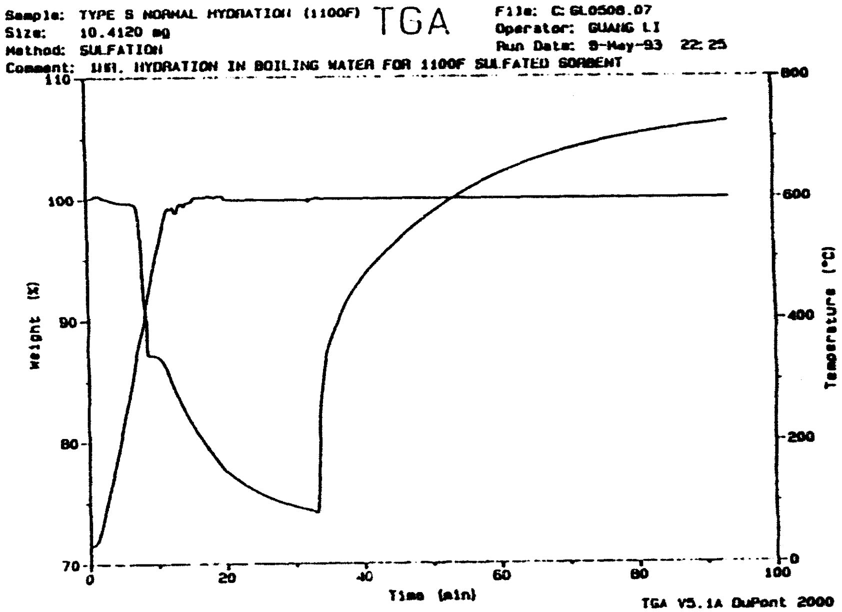
Figure 40. TGA for type S samples pre-injected at 1000°F

Top: after primary injection

Top Right: after atmospheric hydration

Right: after pressurized hydration





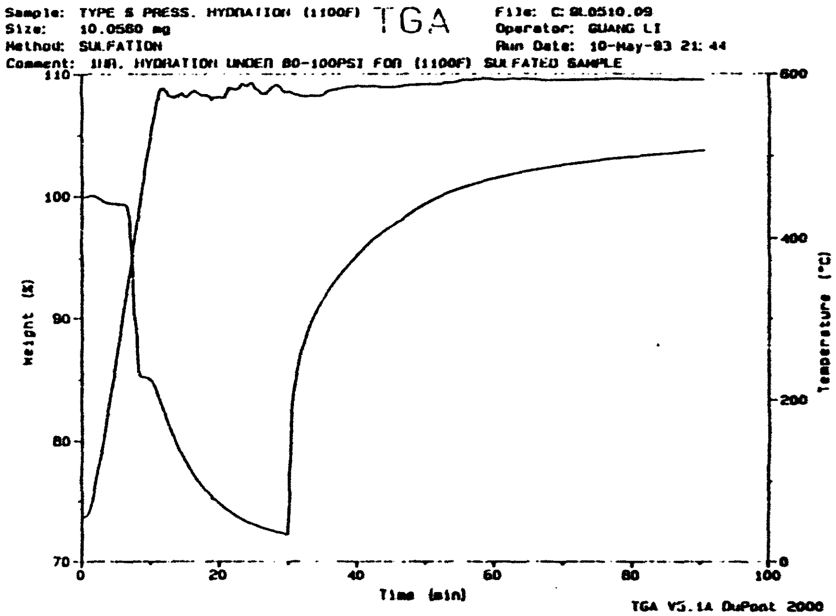
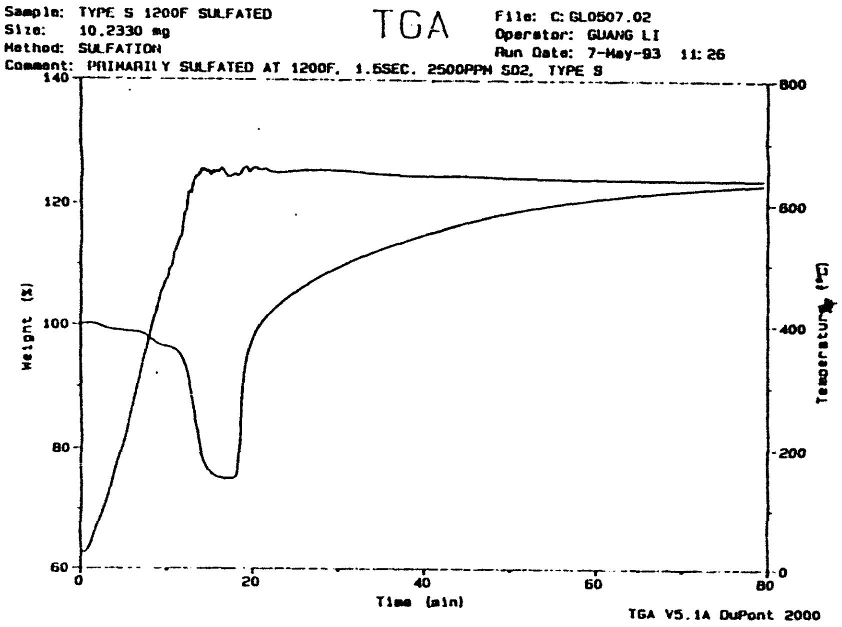
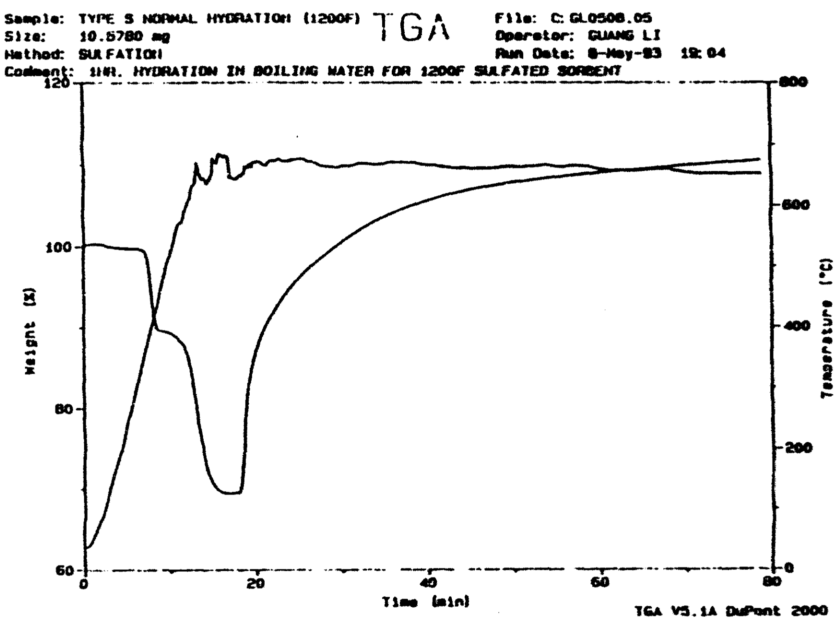


Figure 41. TGA for type S samples pre-injected at 1100°F

Top:	after primary injection
Top Right:	after atmospheric hydration
Right:	after pressurized hydration





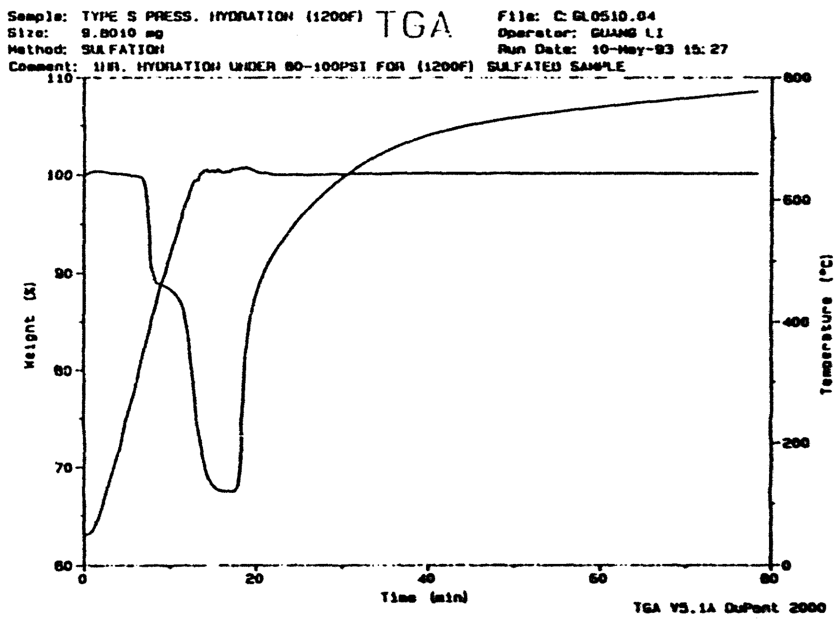


Figure 42. TGA for type S samples pre-injected at 1200°F

Top:	after primary injection
Top Right:	after atmospheric hydration
Right:	after pressurized hydration

loss at this initial heating period under nitrogen environment. This was caused by the decomposition of compounds that were unstable under these temperatures. After a stable weight was reached under that temperature, reactant gas was switched in, which consists of 3000 ppm SO_2, 3% O_2, 14% CO_2 and balance N_2. As a response, a definite weight increase was observed on the TGA curve. One hour later, the reactant gas was cut off and a final weight was marked. Then, a TGA weight increase ratio could be obtained by dividing this final weight by the initial stable weight right before the reactant gas was switched in.

The ratio of weight increase were calculated and listed in Table 2 and Table 3 for samples right after drop tube reaction, Table 4 and Table 5 for samples after atmospheric hydration and pressurized hydration for type N and type S dolomitic sorbents respectively. The summarized weight ration increase are plotted in Figure 43 and Figure 44 for type N and type S dolomitic lime sorbent respectively.

The highest increase in reactivity after hydration treatment was observed for type N dolomitic lime at 1100°F. Recall that this was the temperature that was supposed to be the optimum range for duct injection, it not only had the high sulfation rate in primary injection, but also the low carbonation rate and the high dehydration rate. Large amount of oxides was in the sample prepared at this drop tube temperature, providing very good condition for making use of the hydration method to induce the fracture of spent sorbent particles.

However, this increase was not as significant as it was expected and lots of other hydrated samples showed a decrease in reactivity. It is supposed that the clumping of particles in the drying process after hydration should be responsible for it. Clumping must have caused the decrease in specific surface area, and this in turn caused the decrease in further reactivity. Suitable drying method needs to be developed in order to produce fine particles with large specific surface.

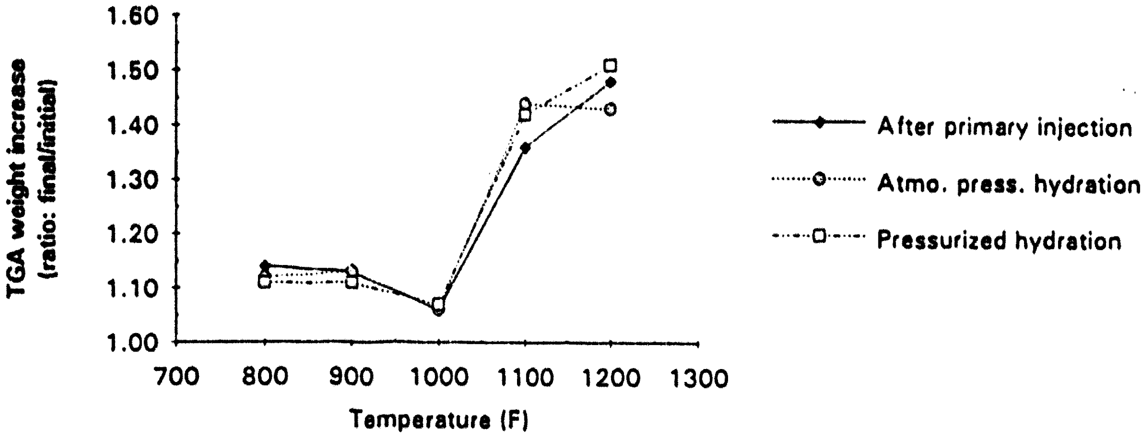


Fig. 31 Test results on further reactivity of type N dolomitic sorbent

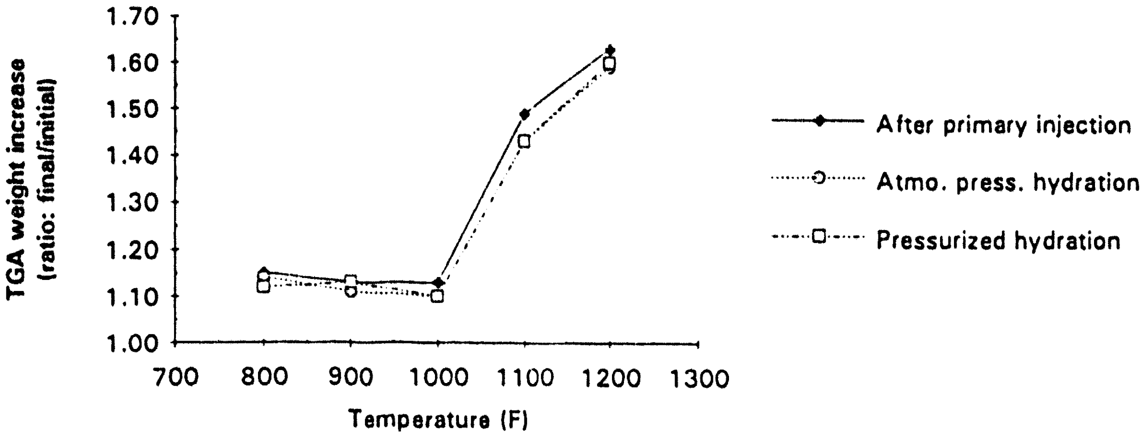


Fig. 32 Test results on further reactivity of type S dolomitic sorbent

H. CONCLUDING REMARKS

The existence of large amount of magnesium in the crystal structure of dolomitic lime gives it special characteristics when used as duct injection sorbent as compared to pure calcium sorbents. One of these that can be taken to advantage is the unique product distribution structure in the used dolomitic sorbent particles. Because of this special structure, available sorbent inside sorbent particles can be recovered by hydration induced sorbent fracture.

The successful recovery of sorbent particles depends on many factors. The reactions between dolomitic sorbent and flue gas in primary duct injection and subsequent collecting processes directly affect the possibility of available sorbent recovery. In addition, methods and factors relating to the process of hydration also determines the efficiency of the process.

A drop tube reactor system was specially built for the study of duct injection reaction mechanism and the preparation of samples for hydration study. This system consists of a main reactor chamber, into which sorbent is injected and well dispersed to allow fast reaction under controlled temperature to simulate the duct injection process, and a collecting filter where the used sorbent is accumulated and allowed to contact with simulated flue gas for prolonged times to simulate the reactions in bag house collectors.

Studies was mainly focused on the samples prepared form the drop tube system with low particle collector temperatures. Carbon, hydrogen and sulfur content of all samples from drop tube system were analyzed in order to understand the reaction process. It has been observed that the hydration content decreased significantly at high temperatures after primary duct injection. Carbonation rate for type S dolomitic lime increased with temperature, but had an extreme value for type N dolomitic lime around 1000°F. A sulfation window was observed around 1000 to 1100°F. 1100°F might be an optimum range for high sorbent usage in primary desulfurization and effective recovery of available sorbent after primary injection.

X-ray diffraction was used to identify the molecular forms of products to assist the understanding of reaction mechanism. The in-complete usuage of sorbent in the primary injection process was evident by the detection of different amount of origional sorbents. Appreciable amount of dehydration and carbonation was observed for all samples, which was consistent with elemental analysis. It is noteworthy that a $MgCO_3$ peak was found in the spectrum of reacted type S dolomitic lime sorbent. This might suggest that $Mg(OH)_2$ was more reactive that MgO under testing conditions. Since carbonation generally compete sorbent with desulfurization processes and reduce the amount of oxides that is essential for sorbent recovery by hydration, this tedency should be avoided.

Both atmospheric hydration and pressurized hydration were tested. It was seen that hydrogen content in the samples increased significantly for both methods. There were definite signs of successful hydration of MgO even though a product shell may have been formed which makes it difficult for SO_2 to diffuse through the outer sorbent particle layer. There were different amount of carbonation happened in hydration process, depending on the extent of contact with air.

Comparative TGA tests were performed to determine the reactivity change before and after hydrations. The highest increase in reactivity after hydration treatment was observed for type n dolomitic lime ar 1100°F. Recall that this was the temperature that was supposed to be the optimum range for duct injection, it not only had the high sulfation rate in primary injection, but also the low carbonation rate and the high dehydration rate. Large amount of oxides was in the sample prepared at this drop tube temperature, providing very good condition for making use of the hydration method to induce the fracture of spent sorbent particles.

The results were promising. However, much more work need to be performed in order to fully determine the conditions of primary injection and subsquent hydration. After this process is fully developed for use in industry, high sorbent utilization can be obtained. In addition, there will be less waste disposal on a per ton of SO_2 reduction basis, which is also desirable for all desulfurization processes.

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