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INTRODUCTION

The purpose of the Brookhaven program is to provide basic process chemistry information required for the development of processes for the utilization and regeneration of lime-based sorbents used in desulfurization of combustion and fuel gases for power production cycles.

Two basic processes for regeneration are currently under development. One is based on the reaction between $CaSO_4$ and carbon for the regeneration of CaO. Another is being designed for regeneration and recycling of the calcium silicates as sorbents, with lime and siliceous matters as the starting materials. The basic reactions involved in the latter process are the formation of silicates from $CaSO_4$ and SiO_2 in the regeneration and the sulfation of the silicates in the combustor.

The two basic processes can be ideally combined in a third system by utilizing the fly ash. Fly ash from the FB combustor contains significant amounts of carbon; about 5-40% from the ANL and the Exxon fluidized bed pilot combustors. By feeding fly ash and sulfated limestone to a kiln-type regenerator, calcium oxide and silicates are formed and are to be recycled to the combustor.

Kinetics and other relevant studies such as particle strength for fluidization and chemical analyses of the products for the three processes are being undertaken in parallel. TGA static systems as well as a micro-pilot system are being used for the kinetic studies. Process and cost analyses are also being made. These include material and energy balances and cost analysis with special attention to the regenerative processes being developed. Results of the studies will serve to guide future experimental work. Kinetic models for sulfation and regeneration are being studied. Models for predicting the behavior of FBC from the bench-scale data are being examined. This paper summarizes the results of this program to date.

EXPERIMENTAL

All the results presented in this paper were obtained with

TGA reactors. A Mettler TA-1, a duPont 951 and a Cahn R 100 were used for the measurements. The reactor systems and the experimental procedures have been described elsewhere.[1-4] A micro-pilot unit is under construction, which consists of a micro-rotary kiln as the regenerator and a small (about 3-inch diameter) fluidized-bed combustor. Kinetic results from this unit would provide a more realistic basis for designing the scaled-up systems.

Materials used in the experiments included in this report will be specified in the following respective sections. The sulfated limestones were either the sulfated Greer limestone from an FBC at Argonne National Laboratory or the Greer stone which was calcined at 900°C in dry N_2 and subsequently sulfated at 900°C with a gas containing 5% SO_2, 10% O_2 in dry N_2. The calcination and sulfation were both carried out in static beds and the sulfation was 65% or 80% complete. Coal ash, silicates and carbon will be described in the respective sections. The grades of the gases were the same as those used previously.[1]

REGENERATION OF CaO WITH CARBON

Basic chemistry for this process is:

$$CaSO_4 + \tfrac{1}{2}C \rightarrow CaO + \tfrac{1}{2}CO_2 + SO_2 \qquad (1)$$

which is a two-step reaction:

$$\tfrac{1}{4}CaSO_4 + \tfrac{1}{2}C \rightarrow \tfrac{1}{4}CaS + \tfrac{1}{2}CO_2 \qquad (2)$$

$$\tfrac{1}{4}CaS + 3/4CaSO_4 \rightarrow CaO + SO_2 \qquad (3)$$

These reactions have been reviewed and studied quite extensively, the results of which are available elsewhere.[1, 5] It has been shown that reaction 2 is much faster than reaction 3, and that the ratio of C/Ca is important in controlling the product (CaO vs. CaS). Ten cycles of sulfation and regeneration (reaction 1) have been tested at 950°C in a TGA system.[1, 5] The up-dated information will be summarized here.

(1) Effect of Temperature on Reaction 3

Reaction 3 is the overall rate-limiting step. The rate of 3 controls the rate of regeneration of CaO. The temperature dependence is presented in Arrhenius fashion in Fig. 1. It is recalled that a surface layer on the $CaSO_4$ is first reduced rapidly by carbon via reaction 2. The reduced layer then reacts with the remaining inner $CaSO_4$ to form CaO via reaction 3. Two distinct slopes on the weight-time curves were obtained in the $CaSO_4 + \frac{1}{2}C$ reaction. The second slope was used to calculate the rates in Fig. 1. The rates here were based on the area of reacting interface, assuming the sulfated Greer limestone particles were perfect spheres. The temperature dependence shown in Fig. 1 is, however, accurate regardless whether this assumption was made, because the same amount of the same materials were used at each temperature.

The activation energy of reaction 3 is 62.7 kcal/mole CaO which indicates a solid-phase diffusion and/or chemical reaction rate-limiting mechanism.

This overall temperature dependence also means that the rate of regeneration of CaO is increased by a factor of three per 50°C rise in temperature in this temperature range.

(2) Effect of NaCl on Regeneration

The effects are demonstrated in Figs. 2 and 3. Figure 2 shows that 3% NaCl (of $CaSO_4$, by wt.) catalyzes both reactions 2 and 3, at 900°C. Figure 3 shows that at 900°C, NaCl first catalyzes reaction 3 but very intriguingly, retards the reaction after about 35% regeneration. However, the results in Fig. 3 were with analytical reagent grade chemicals. As will be shown later, the retarding effect does not take place in the systems containing coal ash and limestone. Also in Fig. 3, the sizes were not specified. The samples were of A. R. grades powder. The $CaSO_4$ was supplied by Baker and CaS was Fisher.

(3) Effect of the Size of $CaSO_4$

In the regeneration scheme, the size of the sulfated stone has to be suitable for fluidized-bed operation while the size of carbon can be small. Figure 4 shows the integrated rates of the two stages (reactions 2 and 3) of the reactions between a partially sulfated Greer lime and coconut charcoal. The integrated rate was based on the total weight loss divided by the total time for each reaction. As shown in this figure, reaction 2 depends strongly on the size of the sulfated stone while reaction 3 has only a very slight dependence on the size. This is understandable because reaction 2 requires close contact between $CaSO_4$ and C whereas reaction 3 does not, and the finer sizes of $CaSO_4$ provide greater contacting areas.

REGENERATION WITH SiO_2

Basic reactions for regeneration and sulfation are:

$$CaSO_4 + SiO_2 \rightarrow CaO \cdot SiO_2 \text{ and } (CaO)_2 \cdot SiO_2 + SO_2 + O_2 \quad (4)$$

$$CaO \cdot SiO_2 \text{ and } (CaO)_2 \cdot SiO_2 + SO_2 + O_2 \rightarrow \text{sulfated silicates} \quad (5)$$

Details of the cyclic reactions are described in reference 1. Sulfation of the silicates has been shown feasible both thermodynamically and kinetically at Brookhaven.

Kinetic data on the sulfation of a monocalcium silicate (low surface area, 99.7% pure, supplied by Research Org./Inorg. Corp.) at various temperatures and SO_2 concentrations have been completed and will be available in our next quarterly report (Jan.-March, 1977). At 900-950°C, on a per weight basis, the rate of sulfation of the silicate is about 40% of the calcined Greer lime. This is partly due to the low surface area. Surface areas were: 2.18 m^2/g for Greer CaO and 0.29 m^2/g for $CaSiO_3$, both calcined at 900°C. Therefore, the silicate appeared to be about 3 times more reactive on a per surface area basis.

REGENERATION WITH COAL ASH CONTAINING UNBURNT CARBON

Based on our data to date, including which to be shown presently, this scheme represents the most practical and attractive process. Numerous experiments have been performed on this system, using partially sulfated Greer limestones from static beds and from Argonne's fluid bed, and coal ash containing carbon that we generated at Brookhaven using small fluidized tubes and the fly ash from Exxon's Miniplant. Argonne's fly ash will also be used shortly.

(1) Reaction Product Analyses

Reactions were carried out between 850 and 1000°C. Ash (carbon content known) with a size of -200+270 mesh (Tyler used throughout) was mixed with partially sulfated Greer limestone of the size -16+20 mesh. The amount of ash was controlled according to the stoichiometry of reaction 1. After each reaction, the ash was sieved out and the stone was analyzed by x-ray diffraction.

The x-ray diffraction analyses to date show that CaO is the predominant product. Trace of $CaSO_4$ was also found. Some CaS was also detected. Some weak-intensity lines indicated the possibility of the existence of the calcium silicates. Our efforts now in this respect are to identify the silicates and to quantify them.

The x-ray results are consistent with the fact that the rates of reaction 1 are higher than the rates of reaction 4. However, at the steady state in a continuous recycling process, the amounts of the silicates would be much higher because for each particle, as it is being recycled, contents of silicates would increase with the number of cycle. This is due to the fact that the silicates stay in the structure once formed.

(2) Rate of Regeneration

Figure 5 shows the rate of regeneration of CaO from a 30% sulfated Greer limestone from Argonne's FBC and a coal ash (Ill. No. 6) containing 7% carbon, at 1000°C. It is seen that more than 90% of the sulfated stone was regenerated within 20 minutes, and about 70% was regenerated in 7 min. On the other hand, using the 65% sulfated Greer limestone that was sulfated at 900°C in TGA reactor, and the same ash and under identical conditions, it took about 3 hrs for 30% regeneration at 900°C. It appeared that the impurities in the FBC sample catalyzed the reaction greatly.

(3) Reactivity of the Regenerated Stone

Preliminary results show that the regenerated stone is more reactive to SO_2. Work is in progress in this area also in physical characterization of the regenerated stone.

(4) NaCl Effect

Rates of regeneration with and without 3% NaCl are shown in Fig. 6. Sodium chloride does catalyze the the regeneration; more so in the initial stage of reaction 3. It does not retard the reaction up to about 60% CaO regeneration. It is possible that the sodium ion serves as a fluxing material in reaction 3.

(5) Effect of the Size of Ash

The effect of the size of $CaSO_4$ has already been shown. Figure 7 shows the effect of the size of ash on rates of reactions 2 and 3. Both reactions are affected strongly by the size. It is not yet understood why reaction 3 has a stronger dependence on the size.

Effect of the carbon content in ash will be investigated.

RELATED STUDIES

(1) Micro Attrition Test

The tests were designed for minute quantities of sample. The fluidizing material is a coarse silica. The sample which has a smaller size is sieved out after the test and its size analysed.

Preliminary results show that the strength of the regenerated sample depends on the amount of $CaSO_4$ remaining. The residual $CaSO_4$ as well as other impurities (not CaO) seem to strengthen the sample.

(2) Mechanism and Fate of NaCl in Sulfation and Regeneration

Details of this study will be presented in our next quarterly report (Jan.-March, 1977). A few important facts are presented here.

In calcining the Greer $CaCO_3$ at 900°C, 3% NaCl decreases the surface area of the CaO. In sulfation, 3% NaCl mixed in the CaO also decreases the surface area of the $CaSO_4$. In either case, about 40% reduction was found. However, the sulfation rate is increased by more than 100%. This rules out the proposition that the effect of NaCl was increasing the surface area and hence increasing the rate

Fate of NaCl in FBC is being studied under simulated combustion conditions in static beds. With 3% NaCl mixed in CaO (reagent grade), sulfated with 0.25% SO_2, 5% O_2 and balance of N_2, the total chlorine was collected by bubbling the off-gas through a NaOH solution. The chlorine content was analyzed colorimetrically and the percentages of the Cl in NaCl that was collected in 2 hrs were as follows: 6% at 800°C, 45% at 850°C, 64% at 900°C and 75% at 950°C. These represented a lower limit because the bubbling depth was only 2 inches and the bubbles were about 1/8 - 1/4 inch in diameter. More careful work is progressing in analyzing and quantitizing the Cl compounds under various conditions.

PROCESS STUDIES

Rigorous process studies are in progress which include cost analyses of various regenerative processes, heat and mass balances, flow sheet investigations, etc.

A preliminary, simplified flow sheet of the regenerative system using fly ash is shown in Fig. 8

Advantages of the process schemes investigated here are as follows:

1. The temperature required in regeneration is lower than that required by the reductive decomposition process using CO. Consequently less deactivation or sintering problems as well as other disadvantages involved in the high temperature (1100°C) operation are caused in the Brookhaven processes.

2. The resultant effluent SO_2 concentration is higher than that of the reductive process using CO because no fluidization is required.

3. Less attrition is involved in the regenerator also because no fluidization is required.

4. For pressurized fluidized-bed combustion, severe limitations arise in the CO-regeneration process because of the high gas flow rate in the regenerator which results in a low SO_2 concentration. For example, at 1100°C the SO_2 concentration in the dry off-gas from the regenerator is about 12% at 1 atm and 2% at 10 atm, at about 70% conversion.[6] In the Brookhaven processes, the pressure dependence is much smaller, and hence they are more suitable for PFBC.

ACKNOWLEDGEMENT

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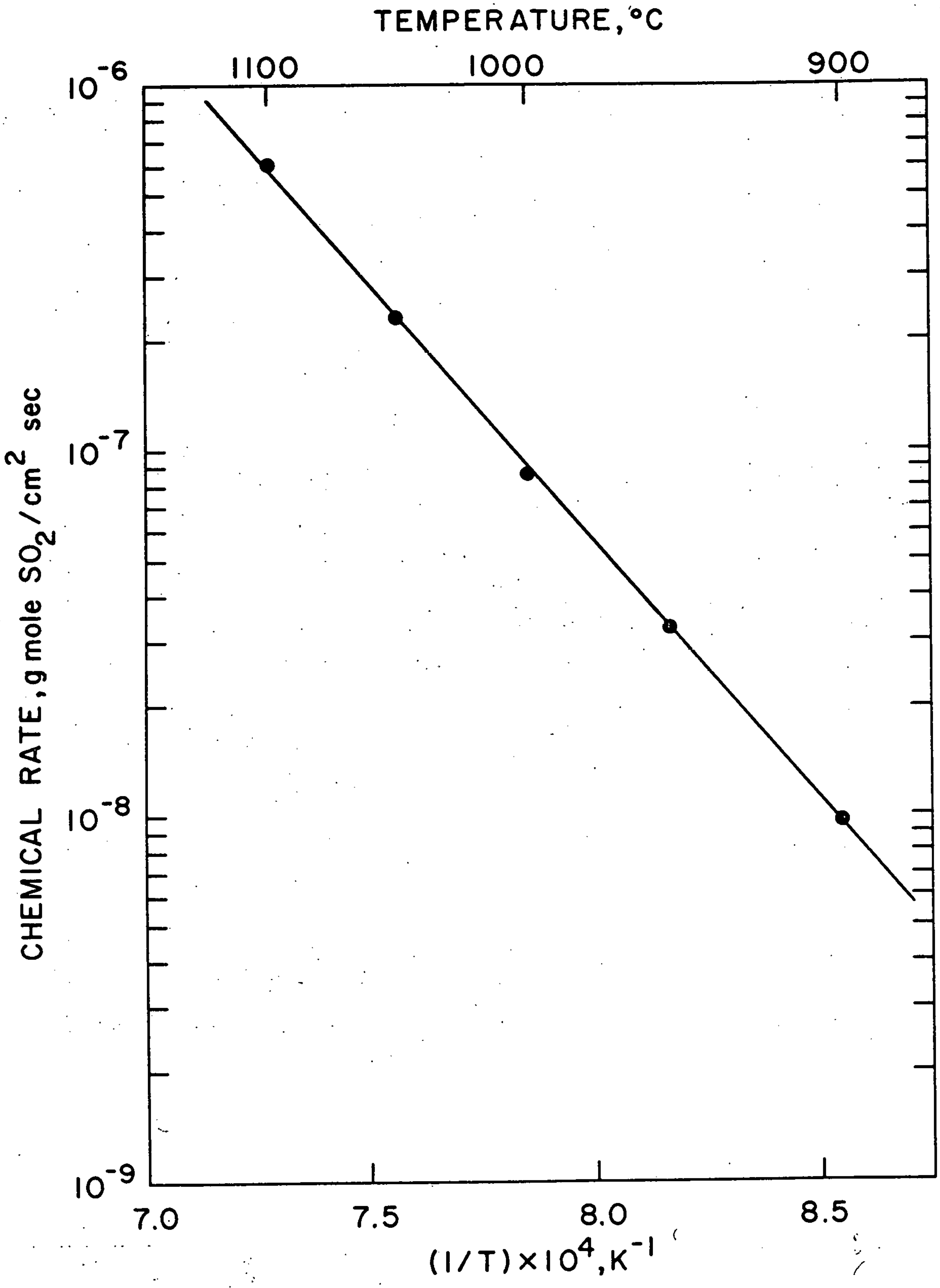


FIGURE 1

RATE OF THE REACTION $3CaSO_4 + CaS \rightarrow 4CaO + 4SO_2$.
80% SULFATED GREER LIME (16/20 MESH) AND COCONUT CHARCOAL
(200/250 MESH) WERE THE STARTING REACTANTS.

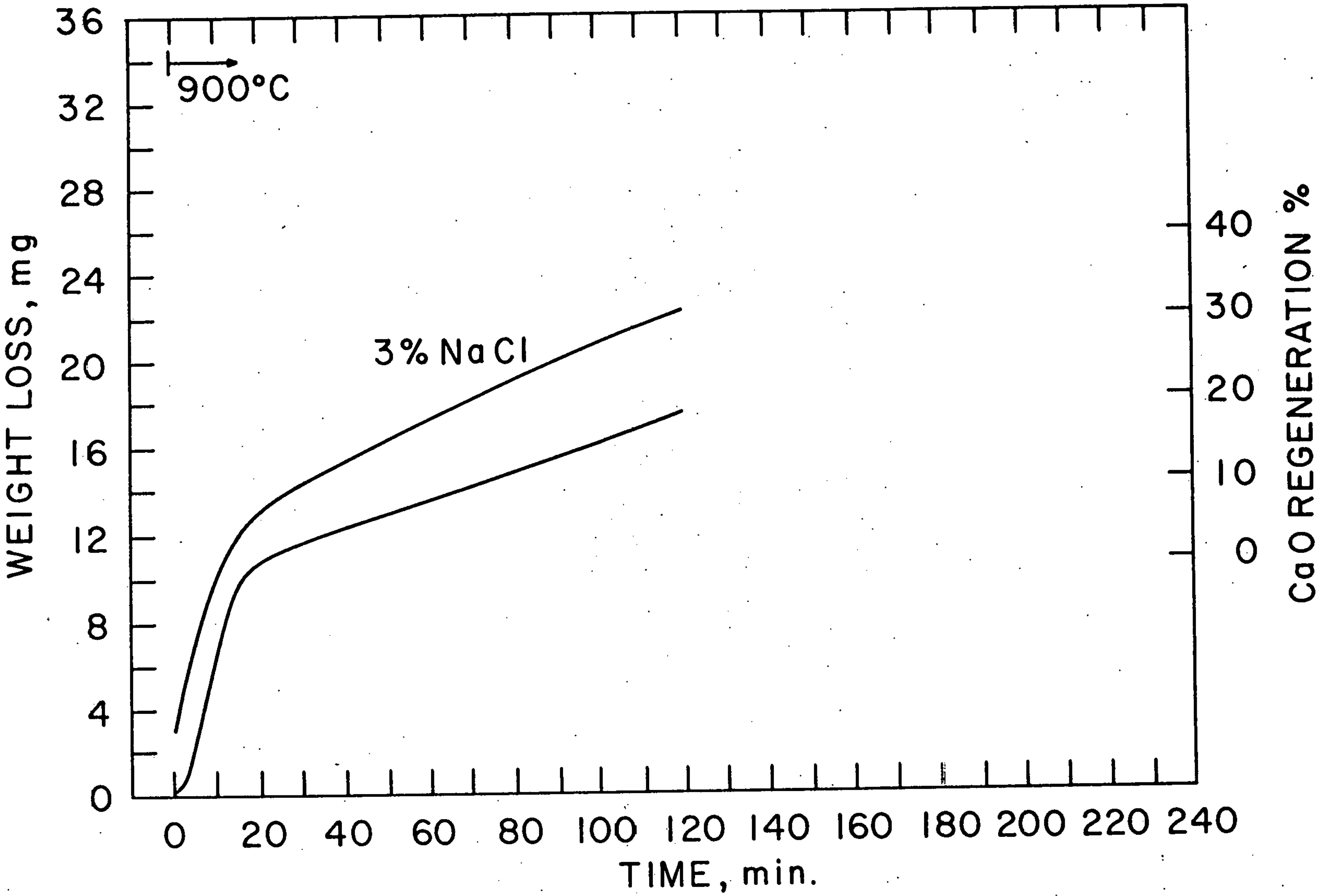


FIGURE 2

REGENERATION RATE WITH CARBON AT 900°C. STARTING MATERIALS: 100 MG 65% SULFATED GREER LIME (16/20 MESH) AND 3.55 MG COCONUT CHARCOAL (200/250 MESH).

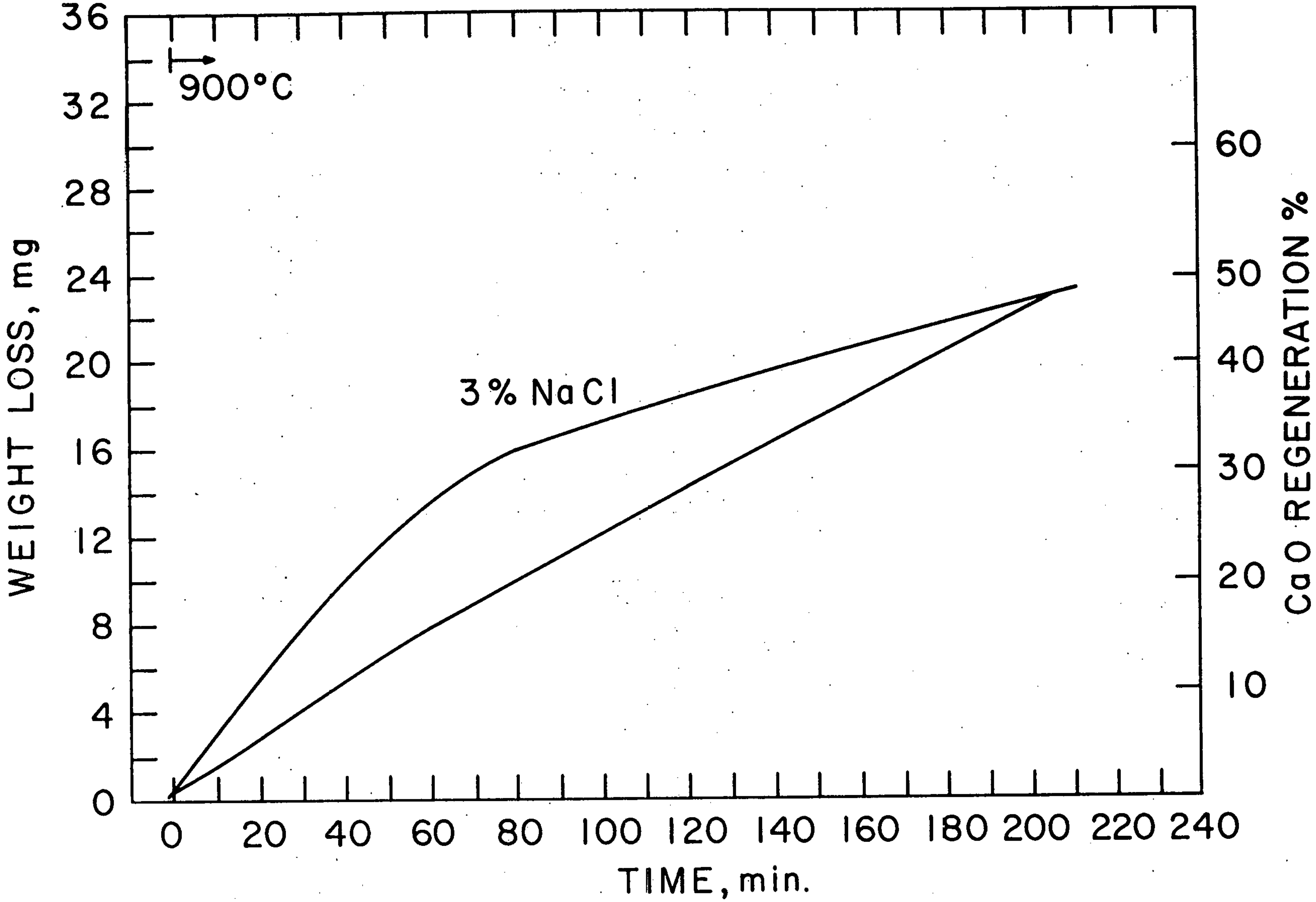


FIGURE 3

RATE OF REACTION $3CaSO_4 + CaS \rightarrow 4CaO + 4\ SO_2$ AT 900°C, WITH POWERED REAGENT GRADE SAMPLES.

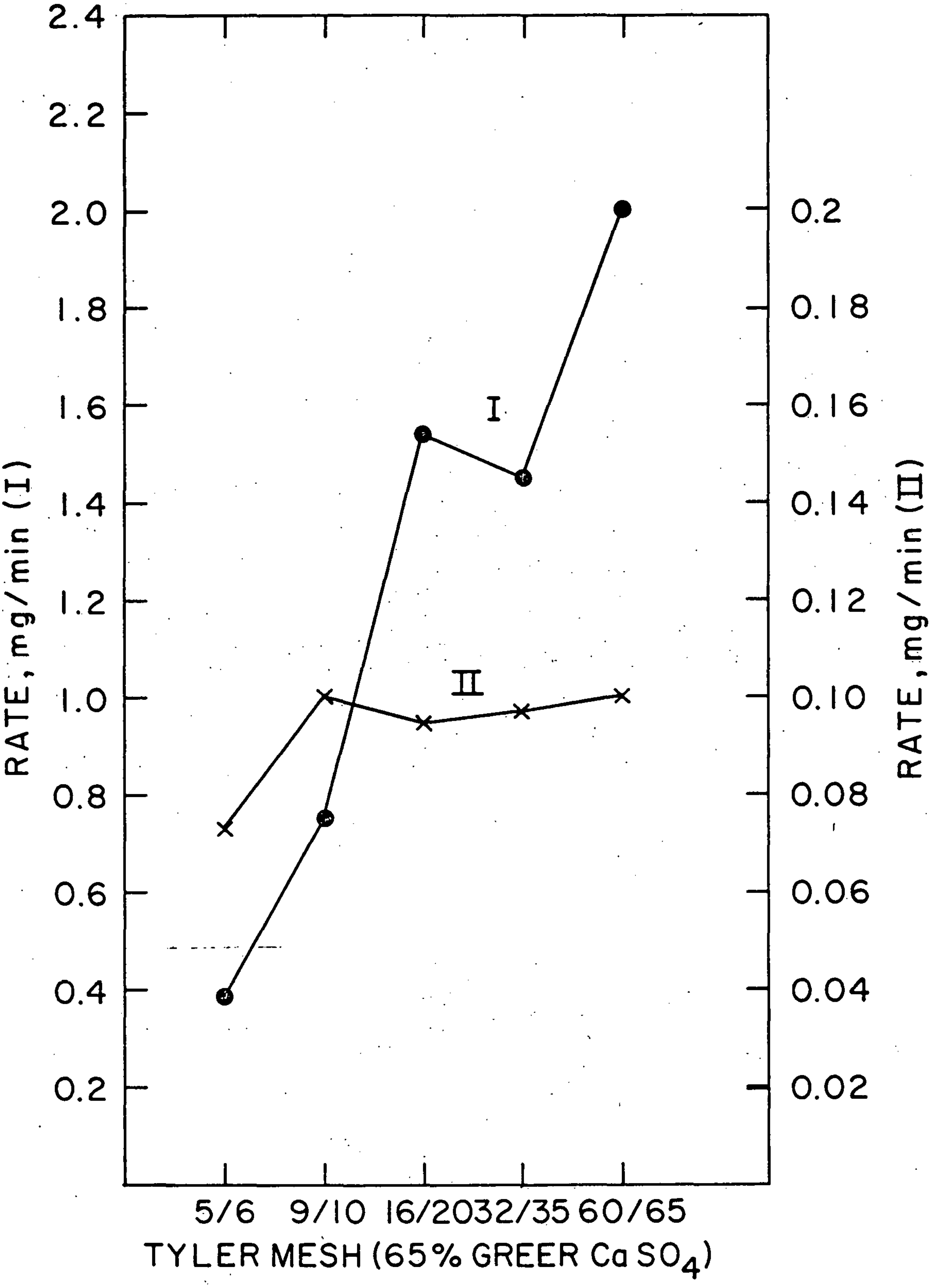


FIGURE 4

EFFECT OF SIZE OF $CaSO_4$ ON REGENERATION AT 900°C.
100 MG 65% SULFATED GREER LIME (16/20 MESH) AND 3.55 MG COCONUT CHARCOAL (200/250 MESH).
I: $CaSO_4 + 2C \rightarrow CaS + 2CO_2$; II: $CaS + 3CaSO_4 \rightarrow 4CaO + 4SO_2$.

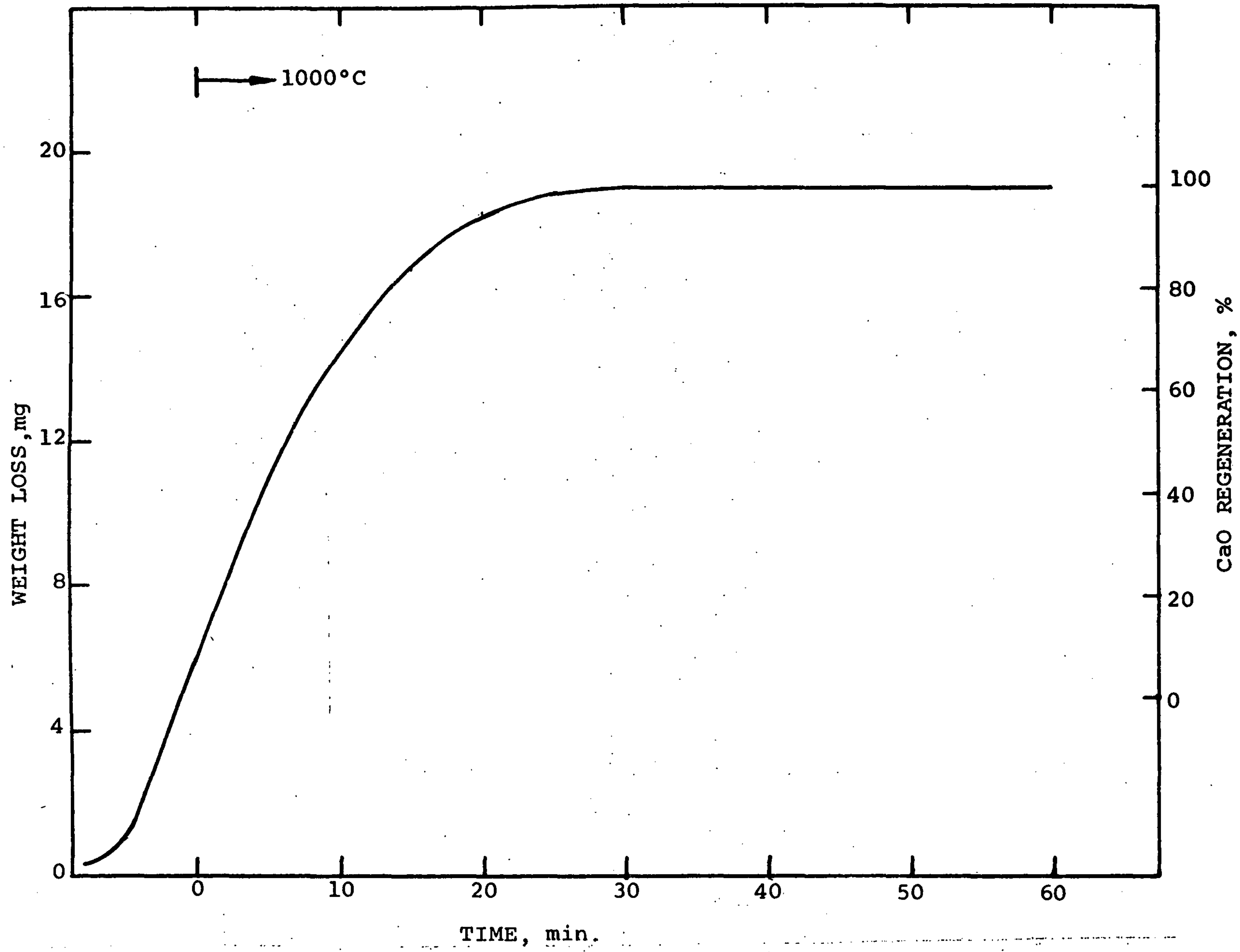


FIGURE 5

RATE OF REGENERATION WITH COAL ASH AT 1000°C. 100 MG 30% SULFATED GREER STONE FROM ARGONNE FBC (SAMPLE J-11202) and 18.9 MG ILLINOIS NO. 6 COAL ASH WITH 7% CARBON (200/270 MESH).

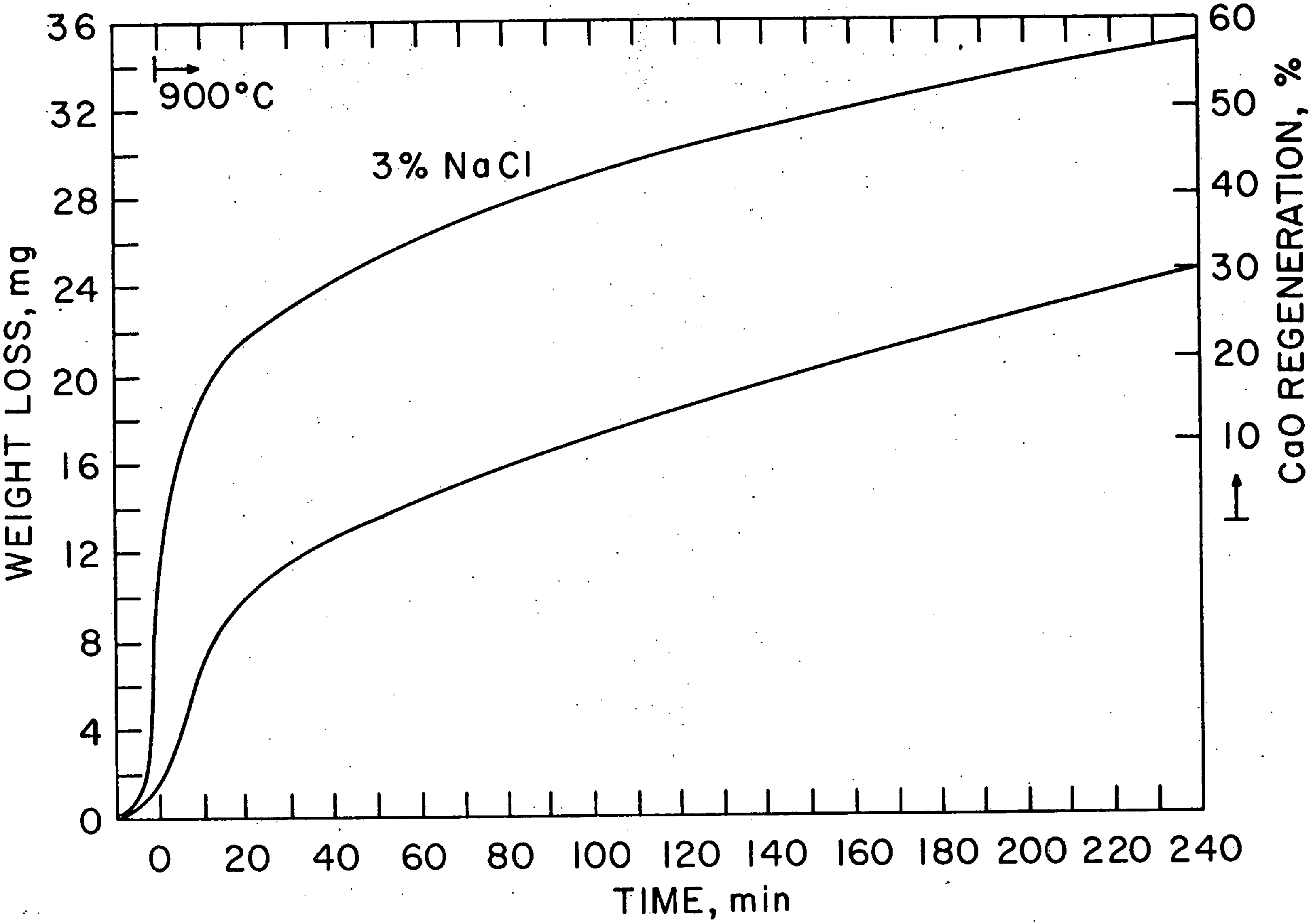


FIGURE 6

RATE OF REGENERATION WITH COAL ASH AT 900°C. 100 MG 65% SULFATED (IN TGA) GREER STONE (16/20 MESH) AND 41 MG ILLINOIS NO. 6 COAL ASH WITH 7% CARBON (200/270 MESH).

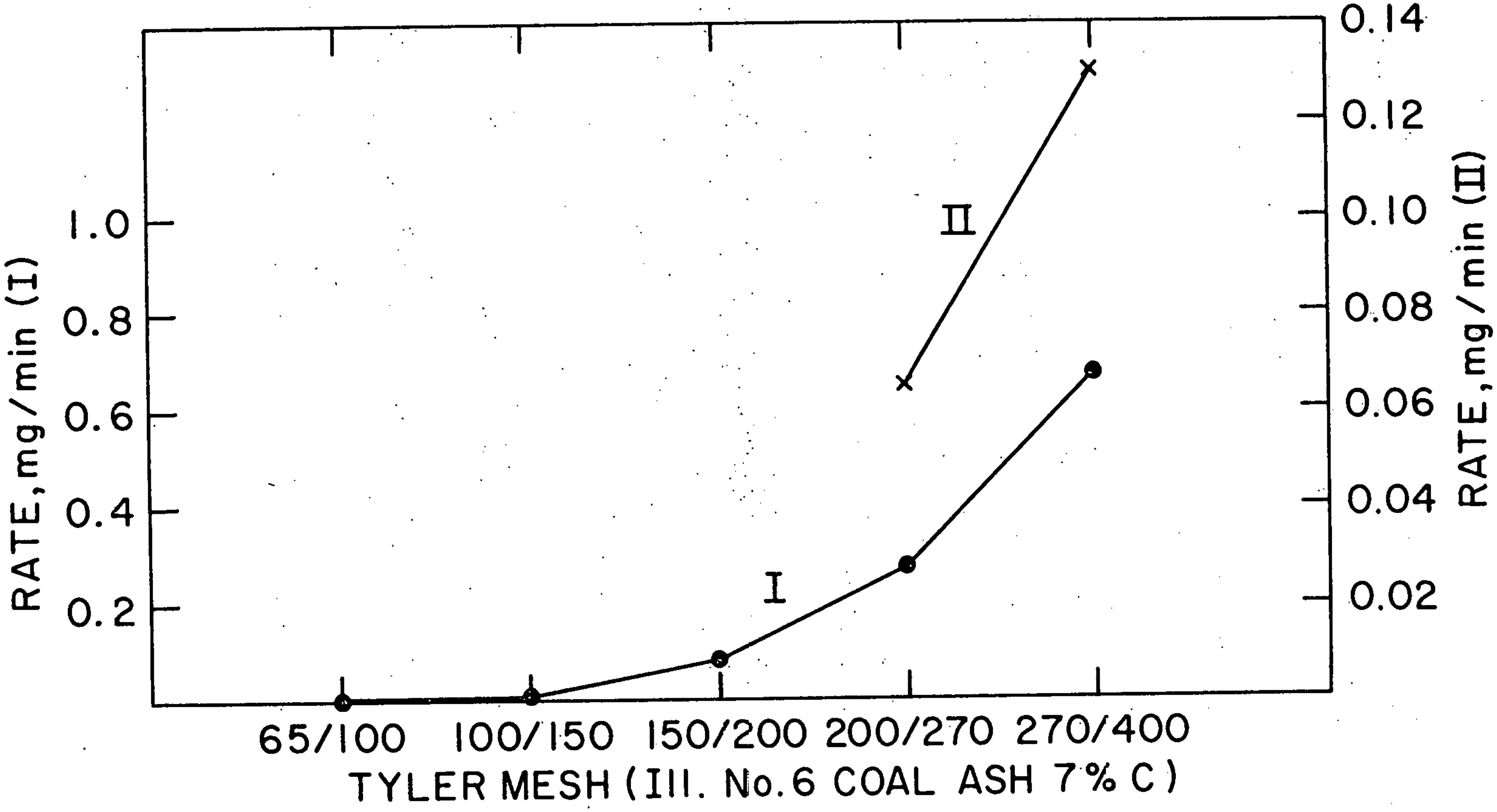
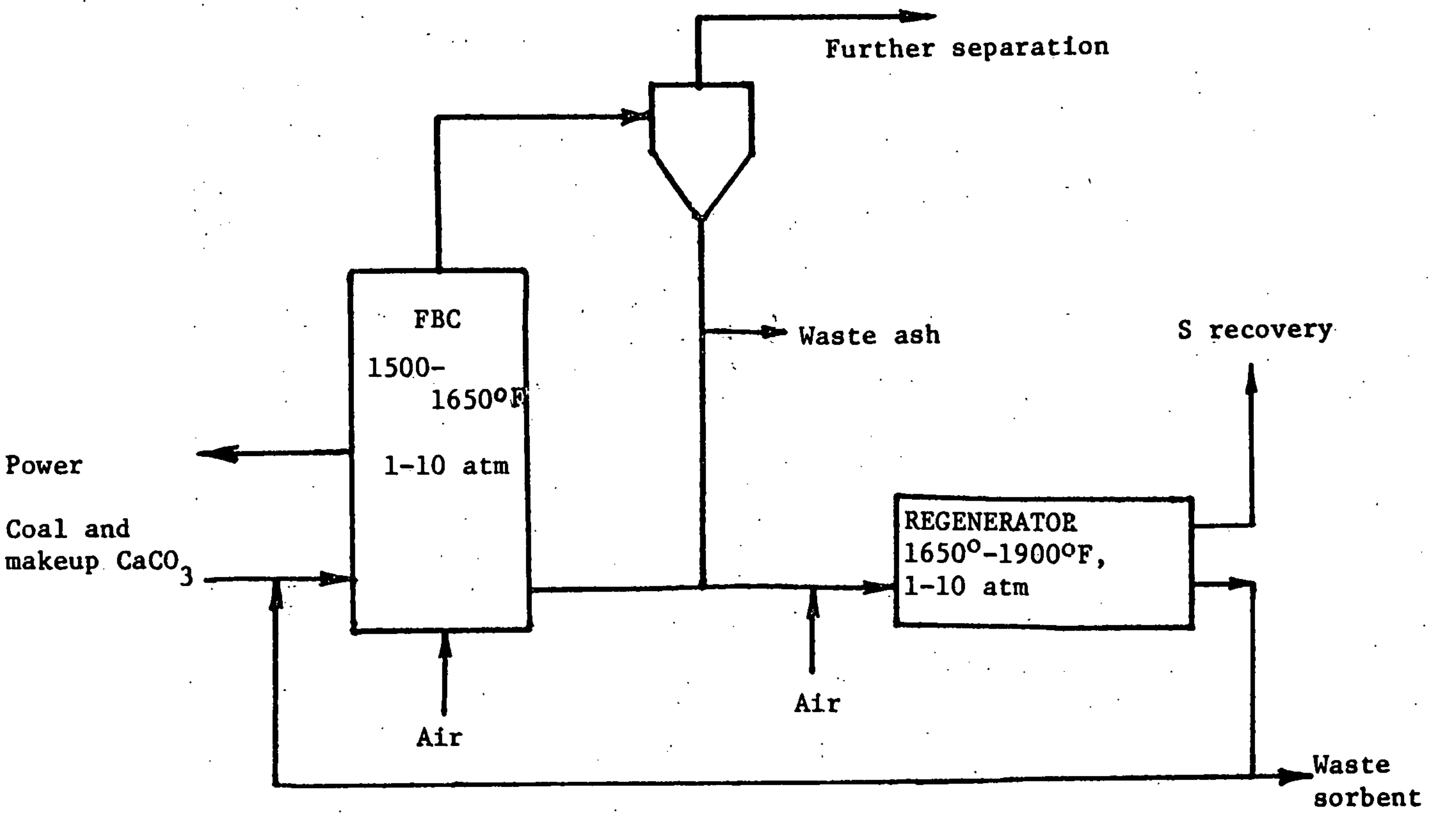


FIGURE 7

EFFECT OF SIZE OF ASH ON REGENERATION AT 900°C.
100 MG 65% SULFATED GREER LIME (16/20 MESH) and 50.7 MG ILLINOIS NO. 6
COAL ASH WITH 7% CARBON. I: $CaSO_4 + 2C \rightarrow CaS + 2CO_2$; II: $CaS + 3CaSO_4 \rightarrow 4CaO + 4SO_2$.

BROOKHAVEN REGENERATIVE HOT GAS DESULFURIZATION PROCESS



In FBC:

Major: $CaO + SO_2 + 1/2O_2 \rightarrow CaSO_4$

Minor: $Ca_xSiO_y + SO_2 + 1/2O_2 \rightarrow$ Sulfated Silicates

In REGENERATOR:

Major: $CaSO_4 + 1/2C \rightarrow CaO + 1/2CO_2 + SO_2$

Minor: Sulfated Silicates + C $\rightarrow Ca_xSiO_y + CO_2 + SO_2$

FIGURE 8