THE USE OF COAL WASTES

FOR THE PRODUCTION OF ALUMINA

Principal Investigator:
H.Y. Sohn
Utah Mining and Mineral Resources
Research Institute
University of Utah
Salt Lake City, Utah 84112-1183

Bureau of Mines Open File Report 139-84

FINAL REPORT

GRANT NO. G1115493
December 1983

Availability: Unlimited

Prepared for
United States Department of the Interior
Bureau of Mines
Washington, D.C. 20241

This is a final report for a grant awarded by the Office of Surface Mining under the Mineral Institutes program of support for graduate education in mineral sciences and engineering. This program was transferred to the Bureau of Mines prior to the completion of the report. The views and conclusions contained in this report are those of the authors and should not be interpreted as necessarily representing the official policies or recommendations of the Interior Department's Bureau of Mines or Office of Surface Mining, or of the U.S. Government.

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REPORT DOCUMENTATION PAGE	1. REPORT NO. BuMines OFR 139-84	2.	3. Recipient's Accession No. PB84-223460
4. Title and Subtitle: The Use of Coal Wastes for the Production of Alumina			5. Report Date: Dec. 29, 1983
			6.
7. Author(s): H. Y. Sohn			8. Performing Organization Rept. No.
9. Performing Organization Name and Address: University of Utah, Department of Metallurgy & Metallurgical Engineering, 412 W.C. Browning Building, Salt Lake City, UT 84112			10. Project/Task/Work Unit No.
			11. Contract(C) or Grant(G) No. (C) (G) G1105089. G1115493, G1195049
12. Sponsoring Organization Name and Address: Office of Assistant Director--Mineral Institutes, Bureau of Mines, U.S. Department of the Interior, Washington, DC 20241			13. Type of Report & Period Covered: University grant, 9/79--12/83
			14.

15. Supplementary Notes

Approved for release July 25, 1984.

16. Abstract (Limit: 200 words)

The primary resource for aluminum at the present time is bauxite. The United States has become more and more dependent on foreign sources for its supply of this strategic material because of its small bauxite resources, which are considered inadequate as a long-range supply. However, domestic low-grade aluminum resources, including coal waste, are considered unlimited. The development of a suitable method for using coal wastes will also alleviate their disposal problems. This report describes three methods of extracting alumina from domestic coal wastes using their carbon contents as a fuel and a reductant of silica contained therein.

17. Document Analysis a. Descriptors

Mining research
Lime-sode sinter process
Carbothermic reduction of alumina to aluminum nitride
Separation of alumina by the volatilization of silica

b. Identifiers/Open-Ended Terms

c. COSATI Field/Group: 08I

18. Availability Statement: Release unlimited by NTIS.	19. Security Class (This Report): Unclassified	21. No. of Pages: 71
	20. Security Class (This Page): Unclassified	22. Price

(See ANSI-Z39.18) See Instructions on Reverse OPTIONAL FORM 272 (4-77) (Formerly NTIS-35) Department of Commerce

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FOREWARD

This report was prepared by the University of Utah under U.S. Bureau of Mines grant numbers G1195049, G1105089, and G1115493. The grant was initiated by the Office of Surface Mining and concluded under the technical direction of the Office of Mineral Institutes, Bureau of Mines with Ronald A. Munson acting as Technical Project Officer. Jeffrey K. Hatfield was the grant administrator for the Bureau of Mines. This report is the final summary of work completed under these grants during the period September 1979 to December 1983. This report was submitted by the authors in December 1983.

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EXTRACTION OF ALUMINA FROM COAL WASTES BY THE LIME-SODA SINTER PROCESS

1.1. Optimum Conditions for Sintering

INTRODUCTION

The primary resource for aluminum at the present time is bauxite. The U.S. has become more and more dependent on foreign sources for its supply of this strategic material because of its small bauxite resources, which are considered inadequate as a long range supply (1), (2). However, domestic low grade aluminum resources, including coal waste, are considered unlimited.

Several methods for extracting alumina as well as recovering other metal values from domestic aluminum-containing materials have been studied (2) - (8). The U.S. Bureau of Mines has been evaluating possible alternatives to the use of bauxite for several years; these include acid leaching and sinter processes applied to clays and anorthosites (9) - (15). Other non-bauxite aluminum resources include fly ash and coal waste. Fly ash from burning regular coals has been widely investigated as a potential supply of alumina (2) - (4), (16). The processes studied for the extraction of alumina from fly ash include variations of sintering and leaching processes (6). On the other hand, the extraction of alumina from coal wastes has been studied very little. Goodboy (17) studied the lime-sinter process applied to coal waste.

A primary concern in this work was the optimization of the different variables involved to give high reaction rates and high recovery of alumina. Coal wastes often give rise to environmental problems affecting air and water qualities as well as land usage. The use of coal wastes for the production of alumina, using its residual fuel during sintering in an environmentally acceptable way, would alleviate these pollution problems.

The sinter process for alumina recovery from alumino-silicate materials involves high temperature reaction of aluminous ore to form a soluble aluminum compound. The sinter is leached to extract the Al_2O_3 and the liquor is subsequently treated to precipitate Al_2O_3 in purified form.

In the lime-soda sinter process, the alumino-silicate ore is reacted with limestone and soda ash at approximately $1200^{o}C$ to form soluble sodium aluminate and insoluble dicalcium silicate. A simplified sintering reaction scheme used by previous investigators to represent this process is:

$$Al_2Si_2O_7 + 4CaO + Na_2CO_3 = 2NaAlO_2 + 2Ca_2SiO_4 + CO_2 \qquad (1)$$

This ideal equation clearly shows the effective separation of alumina from silica with posterior treatment of the products. However, in practice some of the alumina forms various calcium aluminates and calcium-alumino-silicates. To have maximum recovery from the lime-soda sinter, alumina must be extracted from these compounds as well. During the leaching step, separation of the alumina from silica occurs by the dissolution of $NaAlO_2$ in water or dilute Na_2CO_3 solution. According to equation (1) previous investigators concluded that a well burned sinter composed essentially of dicalcium silicate and sodium aluminate is the prerequisite for optimum alumina recovery.

EXPERIMENTAL

Characterization of Coal Wastes

Coal waste samples from the York Canyon Coal Mine, New Mexico, including overburden (OB) material and wastes from the coal preparation plant (PP), were crushed. A representative sample of each one was further ground to -200 mesh and analyzed. Table I shows the results.

Table I. Coal Waste Analysis

Sample	LOI (%)*	Moisture	Carbon
PP	24.3	2.13	14.0
OB	8.4	3.16	0.9

*LOI: Loss on ignition at 700°C including moisture and coal content.

The results of analysis by X-ray flourescence of both coal waste samples are given in Table II. Except for the coal content, both samples, OB and PP, differ little in the inorganic contents. Qualitative mineralogical analysis showed the presence of coal, quartz, muscovite, kaolinite, feldspar, pyrite and other minor constituents.

Table II. X-Ray Fluorescence Analysis of Coal Waste

	PP	OB
SiO_2* (%)	62.2	73.1
Al_2O_3 (%)	22.8	17.9
Fe_2O_3 (%)	3.4	3.9
TiO_2 (%)	0.9	0.8
MgO (%)	1.3	1.4
CaO (%)	1.8	0.3
K_2O (%)	2.8	2.8
MnO (%)	0.03	0.03
P_2O_5 (%)	0.07	0.06

*Percentages correspond to samples burned at 900°C.

Experimental Procedure

Coal waste of -200 mesh, reagent grade $CaCO_3$ and Na_2CO_3 were thoroughly mixed to give predetermined molar ratios of CaO/SiO_2 and Na_2O/Al_2O_3. A sample of 1.2 to 5.0 g was placed in a platinum crucible in a vertical tube furnace. The sample temperature was measured with Pt-Pt 13% Rh thermocouple placed outside the crucible. The samples were burned in air at various temperatures for specified durations. Afterwards the sinter was ground and leached with 3% Na_2CO_3 aqueous solution vigorously agitated for an elapsed time of 40 minutes at 60-70°C. After leaching, the solution was filtered and the filtrate analyzed for aluminum by atomic absorption spectroscopy.

RESULTS AND DISCUSSION

Main variables expected to have significant influence in the sintering reaction or the extraction of alumina are temperature, the composition of the reactants, and sintering time. Determination of the effects of these variables for the same leaching conditions should provide the optimum

conditions during sintering for a high conversion of alumina. Subsequent determination of the leaching variables, temperature, time and lixiviant concentration should establish the optimum conditions for a high alumina yield from coal waste.

SINTERING

Sintering experiments in the range of 1100-1300°C were carried out isothermally to study the effects of the variables using both OB and PP samples. The physical appearance of sinters for different conditions did not change very noticeably; in general, the sinters were friable and porous. Coherent dense mass was observed only at about 1350°C. The sinters melted at about 1360°C.

Effect of Sintering Time

Figure 1 shows the effect of sintering time on the alumina extraction for the preparation plant sample with Na_2O/Al_2O_3 = 1.2 and CaO/SiO_2 = 2.0 at 1150°C. In Figure 2 the combined effect of time and temperature for samples with composition Na_2O/Al_2O_3 = 1.0 and CaO/SiO_2 = 2.0 is shown. The formation of soluble alumina increased with increasing sintering time only at low temperatures, i.e., 1100-1150°C, while at higher temperatures highest alumina recoveries were reached in short durations.

Effect of Temperature

The effect of temperature was studied using both PP and OB samples sintered for 30 minutes. The results are shown in Figure 3. Extraction increased with temperature until about 1250°C. Beyond this temperature, the effect was negligible for the preparation plant sample, while for the overburden sample the highest extraction occured between 1250-1300°C.

Effect of Na_2O/Al_2O_3 Molar Ratio

The results from the study of the effect of soda/alumina molar ratio for a constant lime/silica ratio are shown in Figure 4. The optimum range corresponds to soda/alumina ratios of 1.2-1.3. Ratios greater than 1.3 are not necessary and in fact they seem to be harmful. This is believed to be due

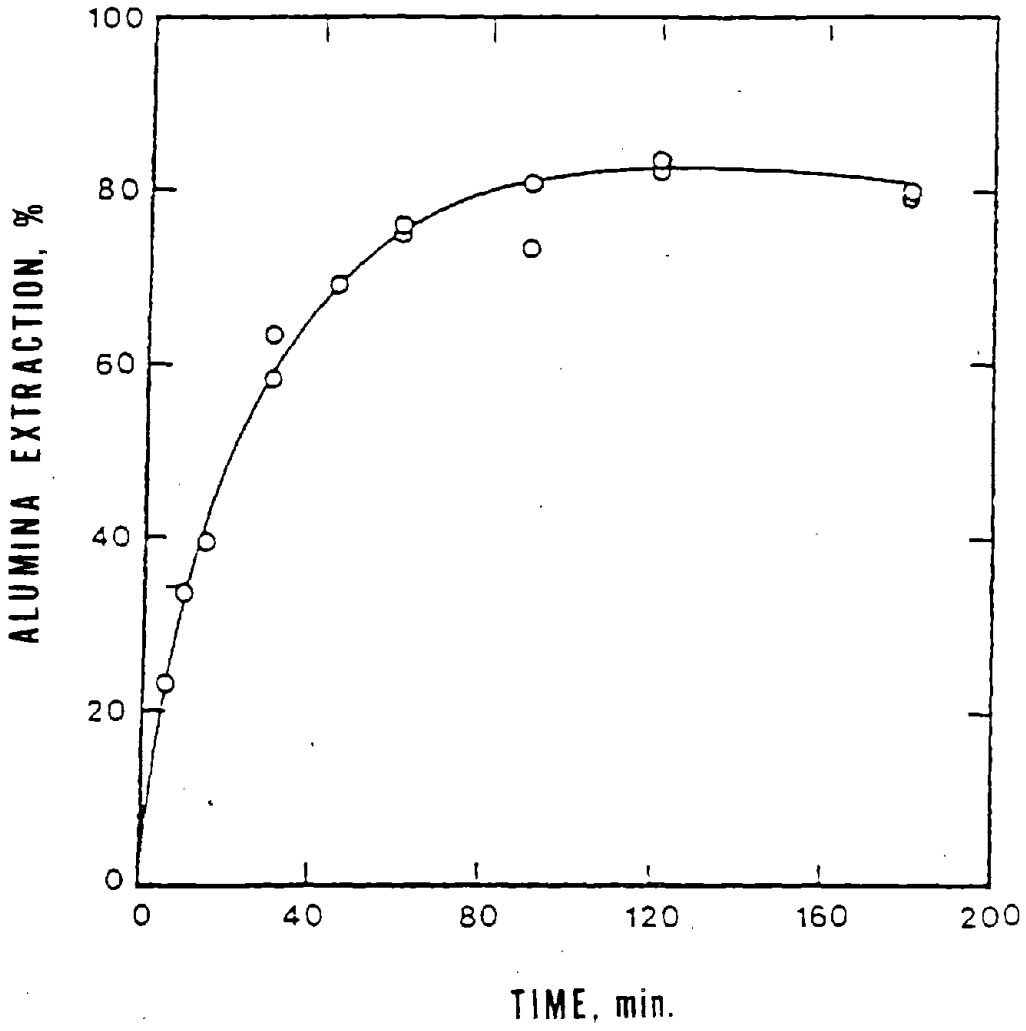

Fig. 1. Effect of sintering time on alumina extraction for a preparation plant sample (Temperature = 1150°C; Na_2O/Al_2O_3 = 1.2; CaO/SiO_2 = 2.0).

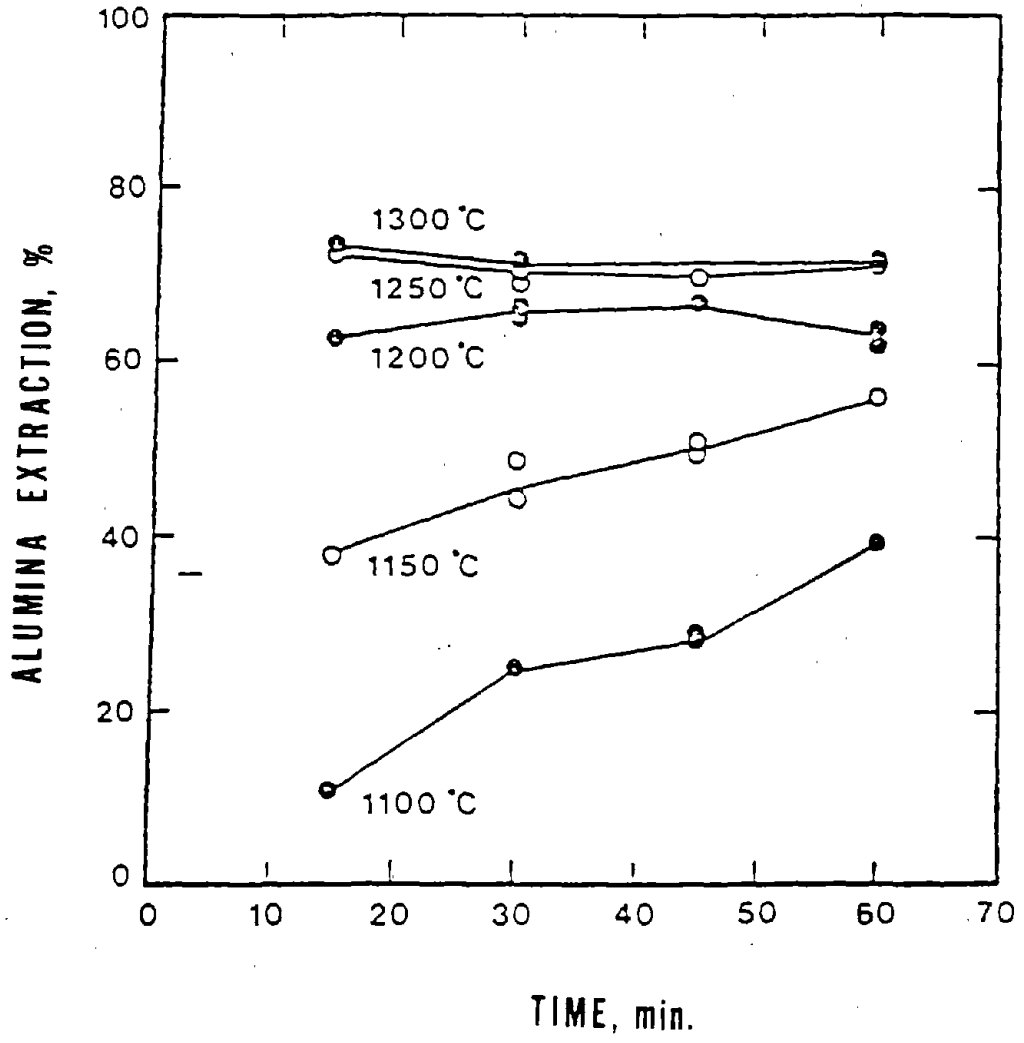

Fig. 2. Effect of sintering time on alumina extraction for a preparation plant sample (Na_2O/Al_2O_3 = 1.0; CaO/SiO_2 = 2.0).

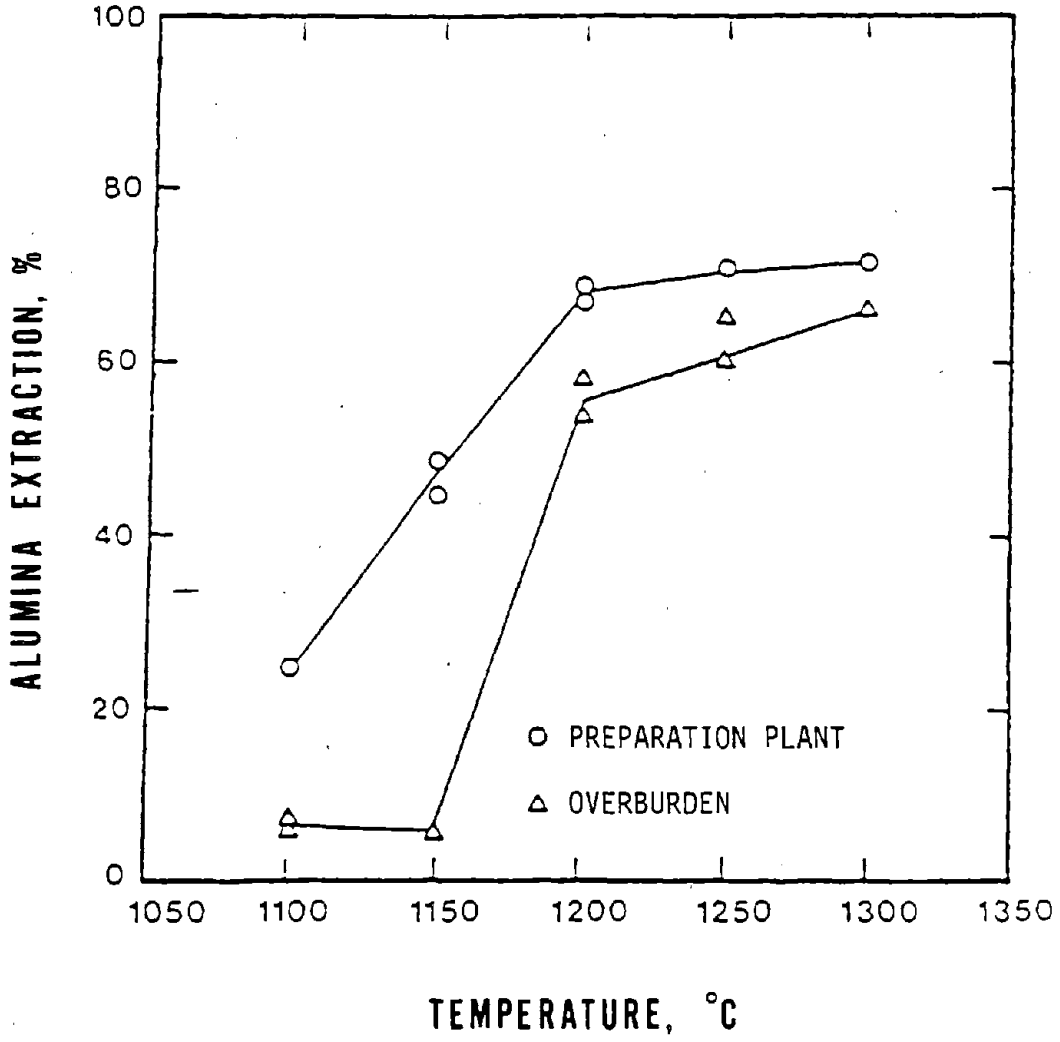

Fig. 3. Effect of temperature on alumina extraction (time = 30 minutes; Na_2O/Al_2O_3 = 1.0; CaO/SiO_2 = 2.0).

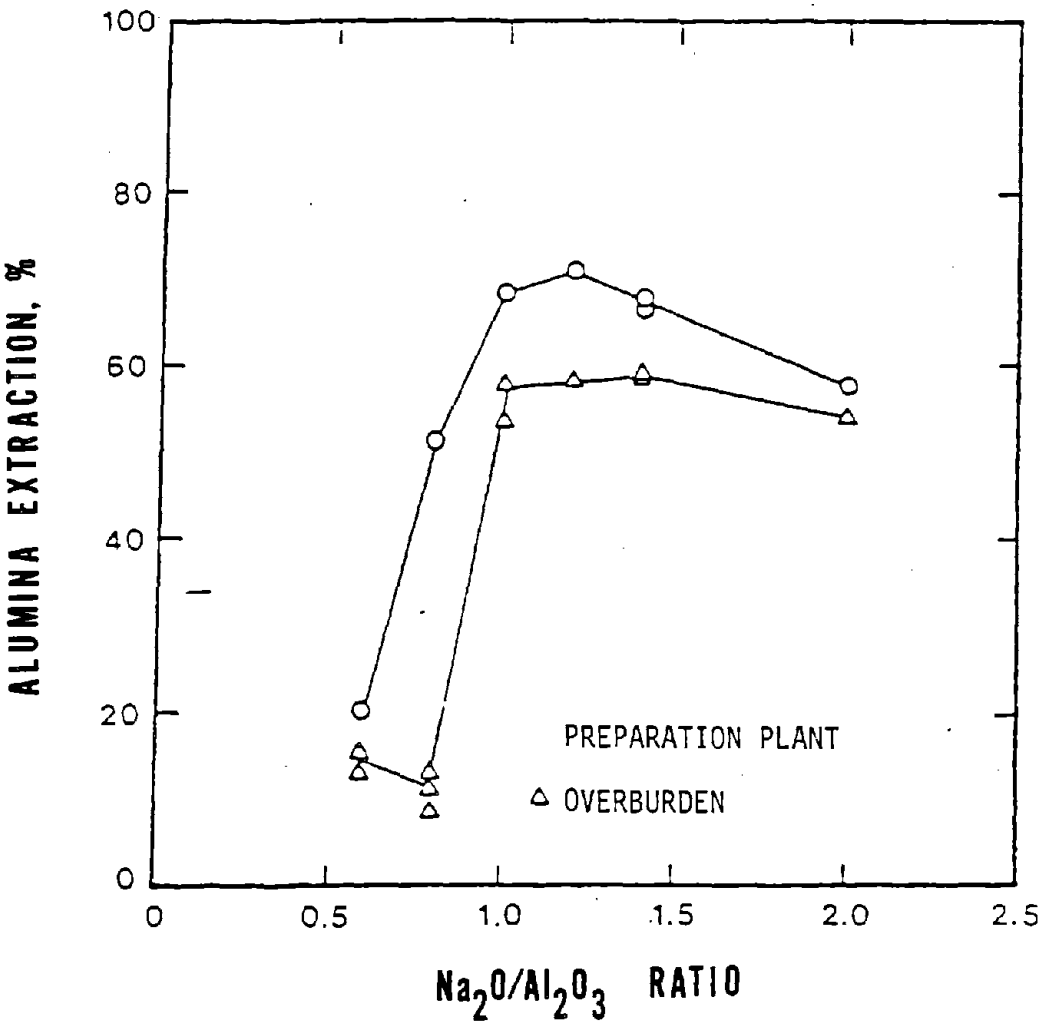

Fig. 4. Alumina extraction as a function of Na_2O/Al_2O_3 molar ratio (Temperature = 1200°C; time = 30 minutes; CaO/SiO_2 = 2.0).

to the formation of some insoluble compound between soda and alumina.

LEACHING

Leaching variables were investigated in the range of 25-85°C using sinters with Na_2O/Al_2O_3 = 1.2 and CaO/SiO_2 = 2.0 burned at 1250°C for 30 minutes.

Effect of Leaching Time.

Extraction of alumina increased slowly with leaching time at 25°C, but at 72°C extraction did not increase appreciably with time (See Figure 5). In fact, in very short durations of approximately 10 minutes, at 72°C, all of the extractable alumina was dissolved.

Effect of Temperature.

The effect of leaching temperature can be seen in Figure 6. The optimum temperature was about 60°C. Beyond this temperature the effect was negligible.

Effect of Na_2CO_3 Concentration.

In Figure 7, the effect of Na_2CO_3 concentration of the lixiviant on the alumina extraction at 72°C is shown. Extraction increased slightly with Na_2CO_3 concentration up to 5%. Extraction remained the same beyond this concentration.

Theoretically, the lime soda sinter process converts the alumina in the silica-matrix material into a soluble compound $NaAlO_2$ and the silicon into Ca_2SiO_4. However, the formation of other compounds of alumina such as $CaO \cdot Al_2O_3$ and $3CaO \cdot Al_2O_3$ also occurs. The monocalcium aluminate, which has varying solubility in Na_2CO_3 solutions depending on the concentration, is the most important of these. Lundquist and Leitch (18) found that $Al(OH)_3$ precipitates out of $CaO \cdot Al_2CO_3$ aqueous solution, if deficiency of OH^- ions exist. $3CaO \cdot Al_2O_3$ has some solubility in Na_2CO_3 solution at 70°C, while it dissolves somewhat better at 30°C by hydrolysis (19).

Formation of these calcium aluminates as well as the interaction of other impurities present in the coal waste accounts for the alumina extraction being lower than 90 percent.

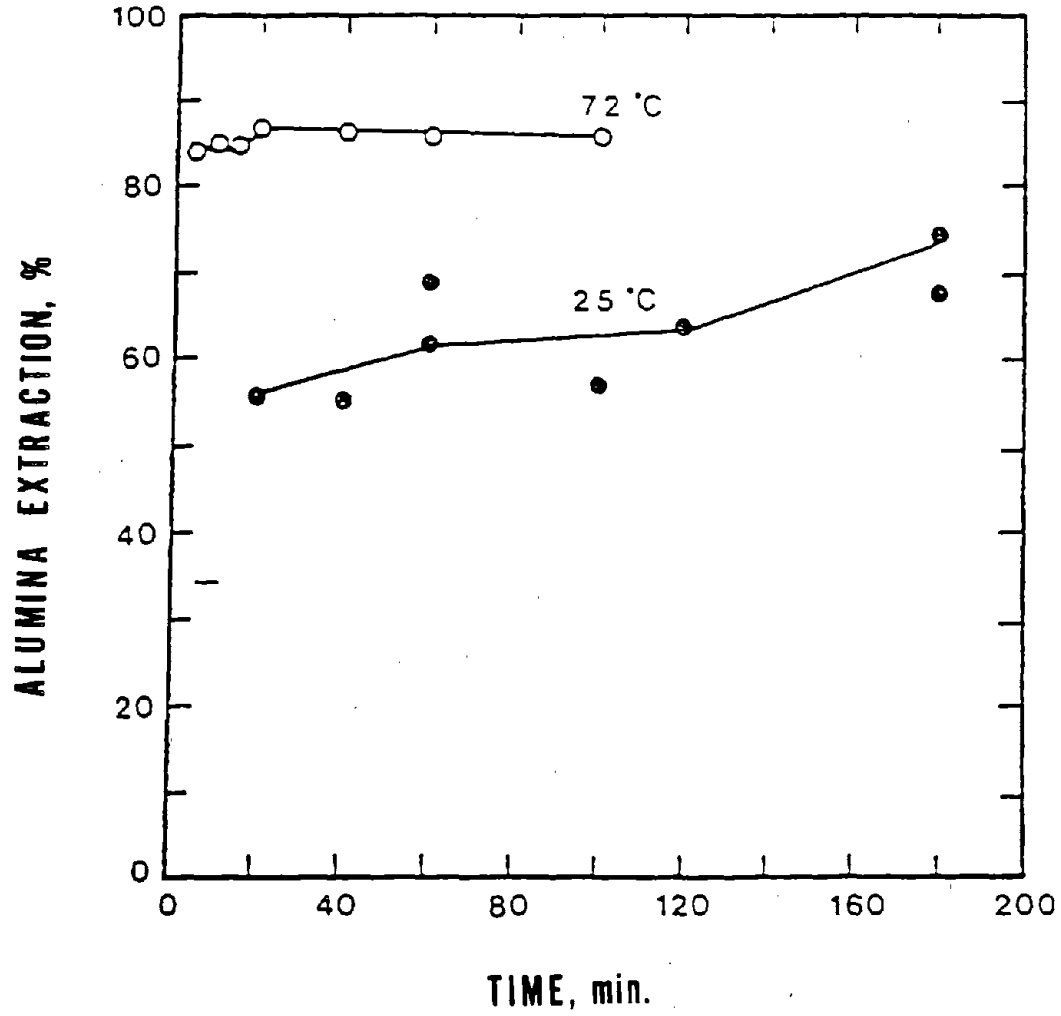

Fig. 5: Leaching time vs. alumina extraction for a preparation plant sample (Na_2O/Al_2O_3 = 1.2; CaO/SiO_2 = 2.0; sintering time = 30 minutes; sintering temperature = 1250°C).

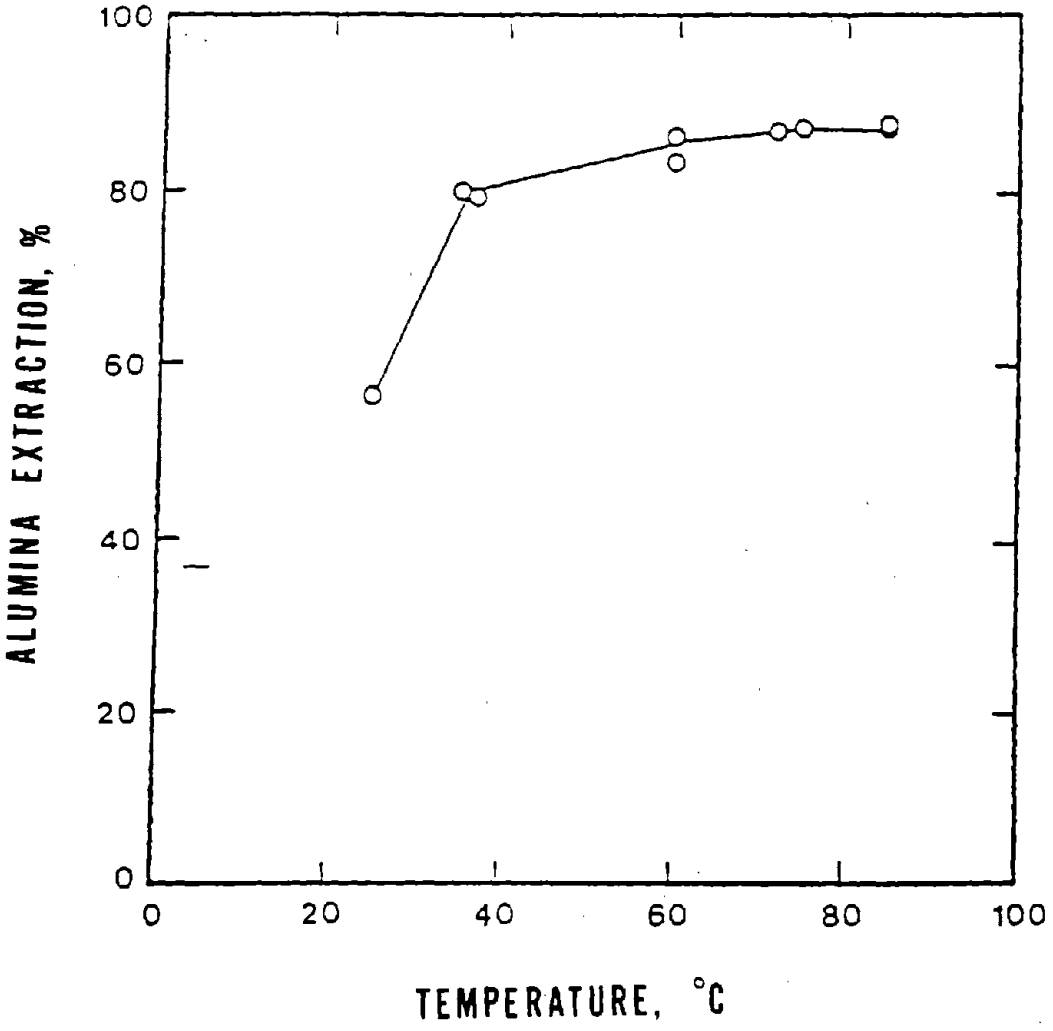

Fig. 6: Effect of leaching temperature on alumina extraction for a preparation plant sample (Na_2O/Al_2O_3 = 1.2; CaO/SiO_2 = 2.0; leaching time = 40 minutes sintering time = 30 minutes; sintering temperature = 1250°C).

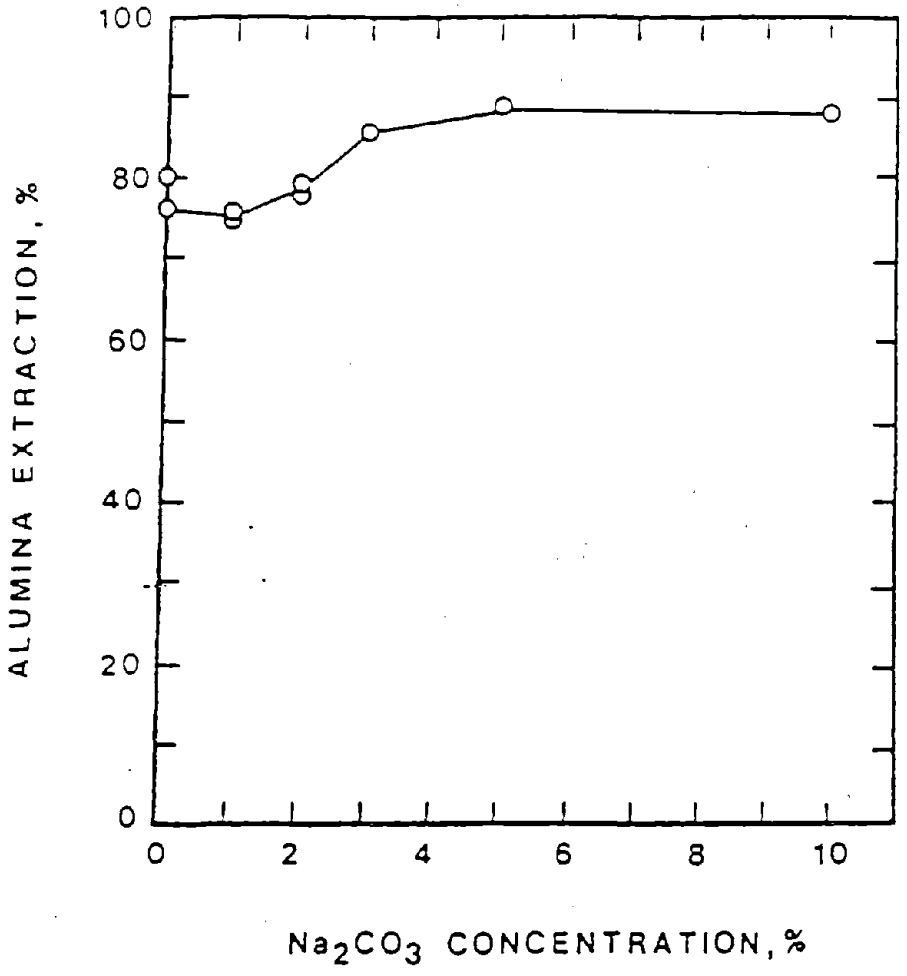

Fig. 7: Effect of Na_2CO_3 concentration of the leaching solution on alumina extraction for a preparation plant sample (Na_2O/Al_2O_3 = 1.2; CaO/SiO_2 = 2.0; sintering time = 30 minutes; sintering temperature = 1250°C; leaching time = 40 minutes; leaching temperature = 72°C).

SUMMARY

Data on the alumina extraction from coal wastes by the lime-soda sinter process indicate that alumina can quite effectively be extracted. Extractions up to 88% were obtained. The optimal conditions for the sintering step were found to be 1250-1300^{o}C for elapsed times of 20-30 minutes and Na_2O/Al_2O_3 ratios of 1.2-1.3. The optimal leaching conditions were determined to be 60-70^{o}C for 20-30 minutes with 5% Na_2CO_3 lixiviant concentration. These favorable extraction results encourage further studies on the development of other operational steps such as desilication (including the removal of other solubilized impurities) and the determination of kinetics.

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Chapter 1 (Continued)

EXTRACTION OF ALUMINA FROM COAL WASTES BY THE LIME-SODA SINTER PROCESS

1.2. Leaching and Desilication of the Sodium-Aluminate Solutions

INTRODUCTION

Extraction of alumina from non-bauxite domestic materials such as coal wastes, clays, and anorthosites has been the objective of many research projects.

In Section 1.1, which has been published in Ref. 1, the extraction of alumina in coal-waste materials by the lime-soda sinter process were described. The reported optimal conditions for the sintering step was 1250° - 1300°C for elapsed times of 20-30 minutes and Na_2O/Al_2O_3 and CaO/SiO_2 ratios of 1.2 - 1.3 and 2.0, respectively. Alumina extractions up to 88 percent were indicated in leaching with 5 percent Na_2CO_3 solutions at 70°C for 30 minutes.

The conventional methods for extracting alumina from sinters include leaching with Na_2CO_3 or NaOH solution, depending on the nature of the raw material used for sinter production and on the sintering process itself. Sodium aluminate and the minor quantities of calcium aluminates formed during lime-soda sinter process dissolve in dilute Na_2CO_3 solutions (1,2). For the high CaO-Al_2O_3 compounds, e.g. $3CaO.Al_2O_3$ and $12CaO.7Al_2O_3$, formed in the lime sinter process, the leach solution must contain an excess of Na_2CO_3 for maximum alumina extraction (3-6).

Although the coal-waste sinter could be leached readily with Na_2CO_3 solutions, the pregnant liquor thus obtained was very difficult to desilicate under various desilication methods and conditions tested.

This section reports on the study of leaching of the solid sinter with caustic solution and water and of desilication of the leach liquor obtained in the lime-soda sinter process applied to coal wastes. The liquor obtained from caustic leaching was found to be quite amenable to desilication.

Two methods for removal of silica from sodium aluminate solutions have been used widely in previous investigations: (i) digestion of the solution at high temperature and high pressure, and (ii) digestion of the solution with certain chemical agents at high temperature and atmospheric pressure.

In the high-pressure digestion method, the conditions of the desilication process vary among investigators from a simple digestion of the sodium aluminate to additions of freshly precipitated calcium carbonate and calcium and barium hydrates (2,7,8). On the other hand, in the desilication-at-

atmospheric-pressure methods, calcium oxide seems to be the agent preferentially used to trap the silica from the solution (2,5). Archibald and Nicholson (3) claimed that desilication will occur if the concentration of the hydroxyl ions in the solution is reduced by carbonation and agitation of the solution in the presence of "seed" charge consisting of a mixture of Al_2O_3, SiO_2, CaO, Na_2O and Fe_2O_3 compounds. Recently, Noworyta (9) reported the desilication of sodium aluminate solution with additions of $Ca(OH)_2$ and concluded that there is a certain critical concentration of the $Ca(OH)_2$ below which the solution does not undergo desilication.

EXPERIMENTAL

Coal waste sinters obtained by the lime-soda sintering described in the previous section were used to study the alumina extraction in water and NaOH solutions. Stock solutions of NaOH were prepared for leaching of finely ground sinter (-100 mesh). Leaching experiments were carried out in a Teflon beaker for specified durations and temperatures under constant agitation. Then the slurry was filtered and the filtrate was analyzed by atomic absorption spectroscopy for its alumina and silica contents.

Desilication tests were performed on the sodium aluminate liquor under atmospheric pressure. $Ca(OH)_2$ was used as the chemical agent. A suspension of $Ca(OH)_2$ in water was added to the sodium aluminate liquor and kept for specified durations under predetermined temperature. The desilication product at the end of the run was filtered and the filtrate analyzed by atomic absorption spectroscopy to determine compositions and to permit calculations on the percentages of Al_2O_3 and SiO_2 precipitated during this process.

RESULTS AND DISCUSSION

The leaching tests were designed to compare the solubility of the alumina compounds in water and NaOH solutions as well as the desilication of the sodium aluminate solutions. Determination of the effects of leaching time, temperature, and concentration and type of lixiviant should provide the optimum conditions for alumina extraction from coal-waste sinters. Furthermore, determination of the effects of desilication variables, time, reagent concentration and temperature should provide the optimum conditions

for a high alumina yield.

Leaching

The first variable investigated in the sinter process was the NaOH concentration of the lixiviant. This set of experiments was run at 70°C and for an elapsed time of 40 min. The results can be seen in Figure 1. Alumina extraction with dilute caustic solution was comparable to extraction with sodium carbonate solutions (1) and water. Figure 1 also shows that alumina dissolution is independent of NaOH concentration. However, silica dissolution increases considerably with increase in NaOH concentration. The lowest dissolution of silica was observed in leaching with water.

The effect of leaching time is shown in Figures 2 and 3. Leaching by both water and NaOH solutions is completed in a relatively short time, as in the case of leaching by Na_2CO_3 solutions (1); in fact, at about 10-20 minutes almost all of the extractable alumina and silica go into the solution. After that, time has little effect on the dissolution of alumina at both 70 and 25°C; however, silica has a behavior opposite to that of alumina for its concentration decreases with increasing time at both 70° and 25°C. This suggests a direct interaction between silica and alumina in the solution. The initially dissolved silica reacts with Al_2O_3 and Na_2O to form an insoluble compound, until silica approaches the equilibrium concentration. Temperature has little effect on the Al_2O_3 and SiO_2 dissolution in water and NaOH solution as shown in Figures 4 and 5.

The solid/liquid ratio (s/l) was found to have some effect on silica dissolution. This is due to the pH variation of the pregnant solution with change in the s/l ratio. This can be seen in Figure 6 where the silica dissolution curve goes through a minimum at about s/l = 0.2. The pH of the pregnant liquor increases gradually with increasing s/l ratio up to about 12.5 (s/l = 0.2) where it levels off as seen in Figure 7.

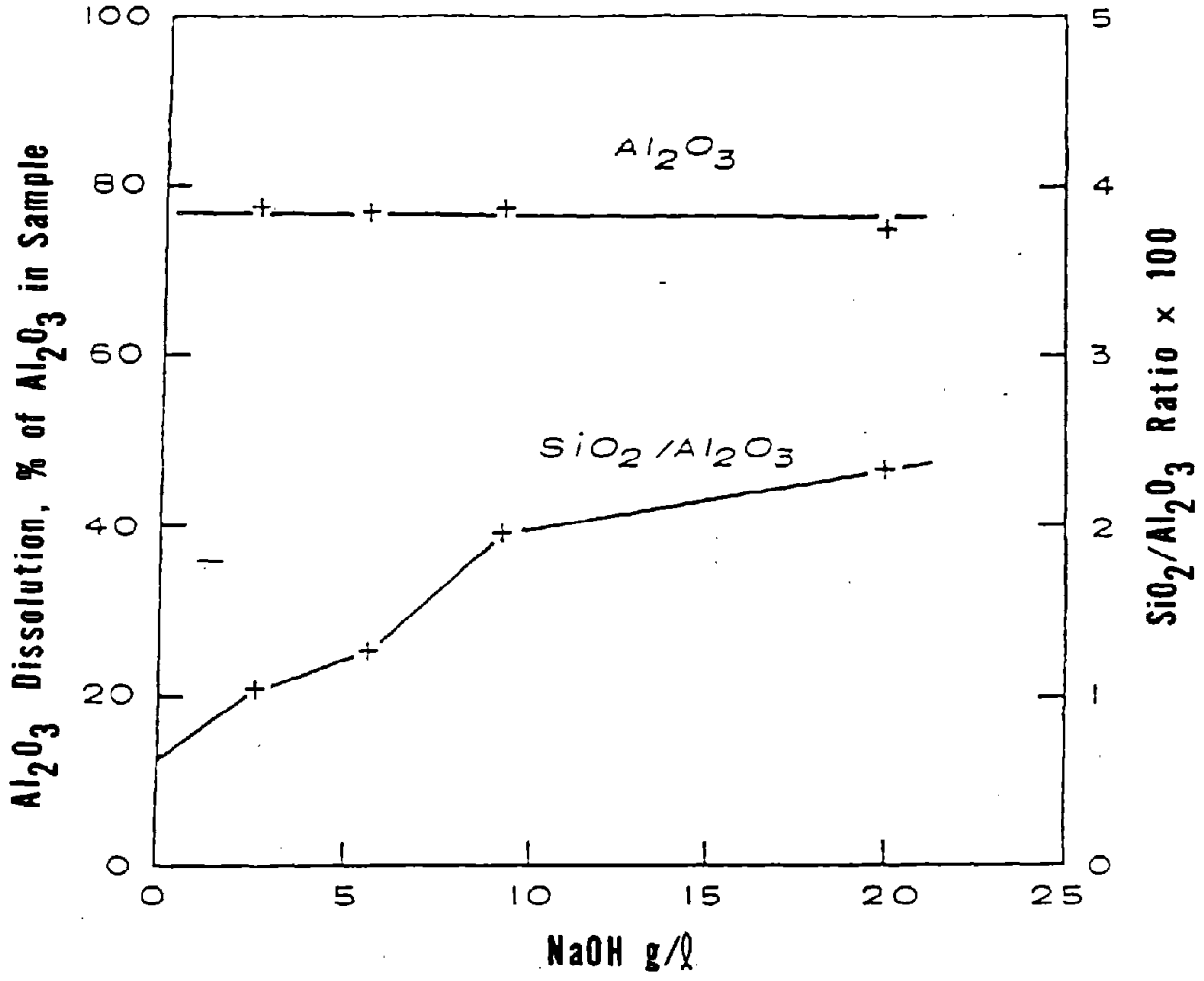

Fig. 1. Effect of NaOH concentration on sinter leaching at 70°C for 40 minutes: solid/liquid ratio = 0.2.

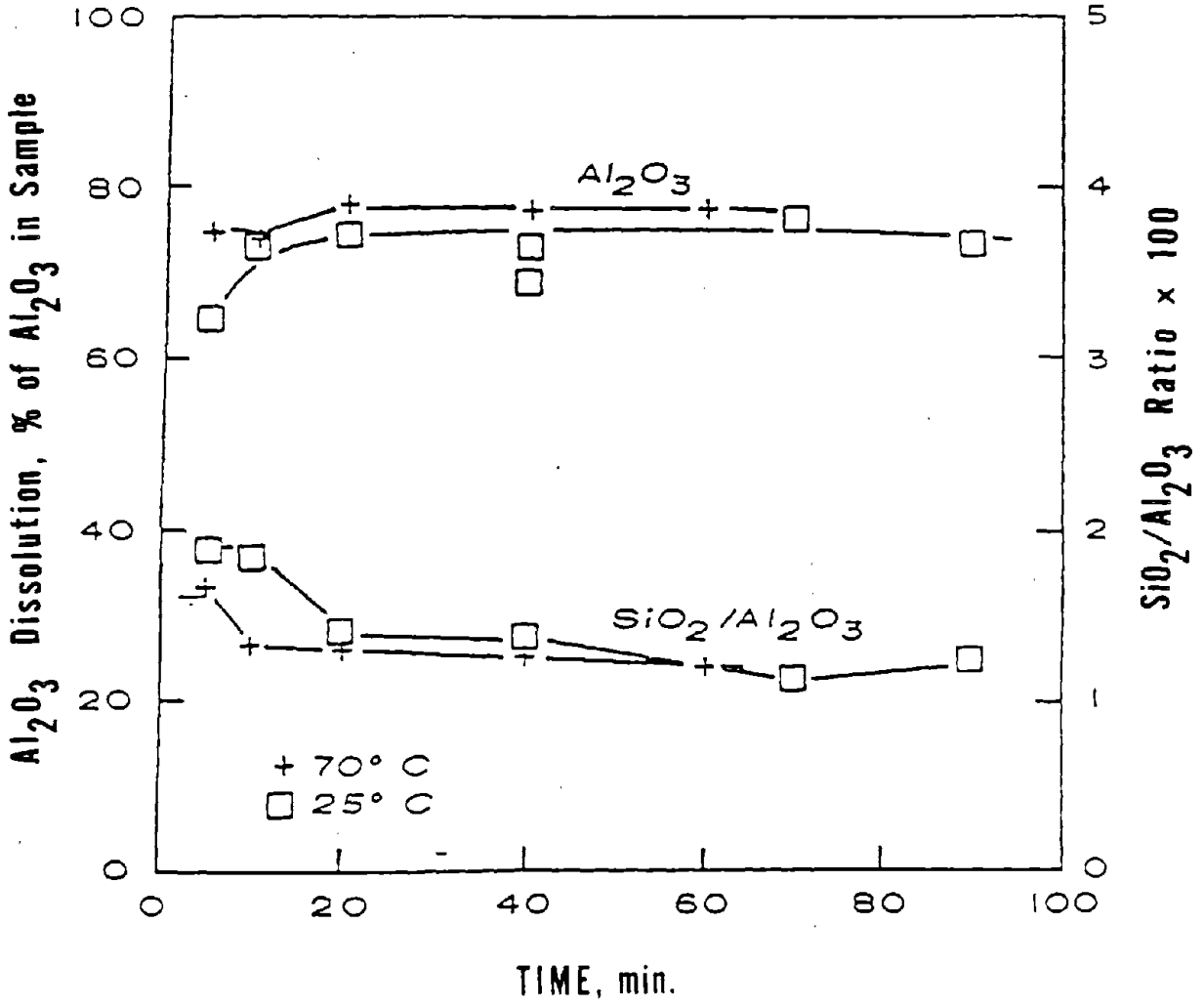

Fig. 2. Effect of leaching time on Al_2O_3 and SiO_2 dissolution at 25 and 70°C in 5.6 g/ℓ NaOH solution: Solid/liquid ratio = 0.2.

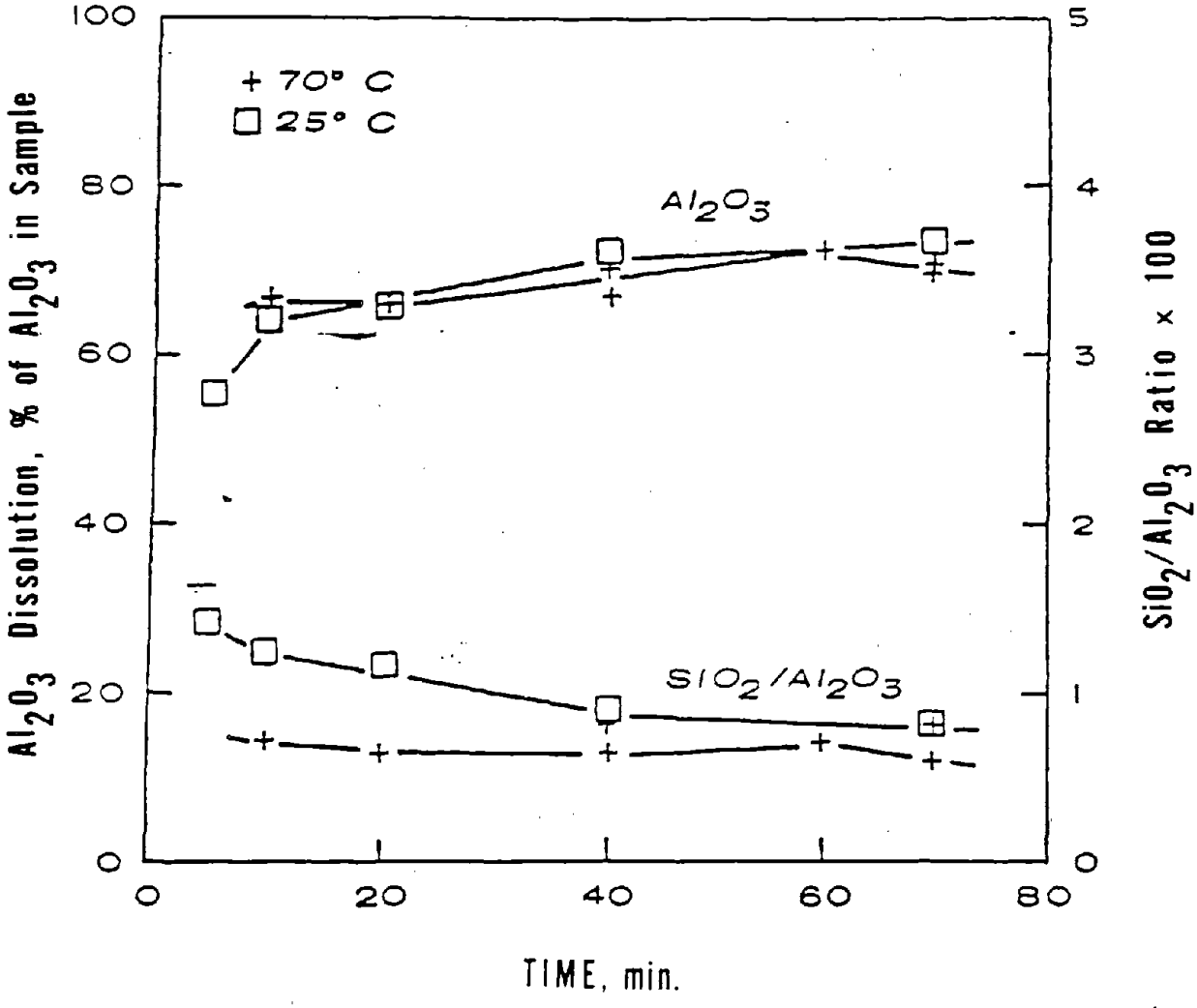

Fig. 3. Effect of leaching time on Al_2O_3 and SiO_2 dissolution at 25 and 70°C in water: solid/liquid ratio = 0.2.

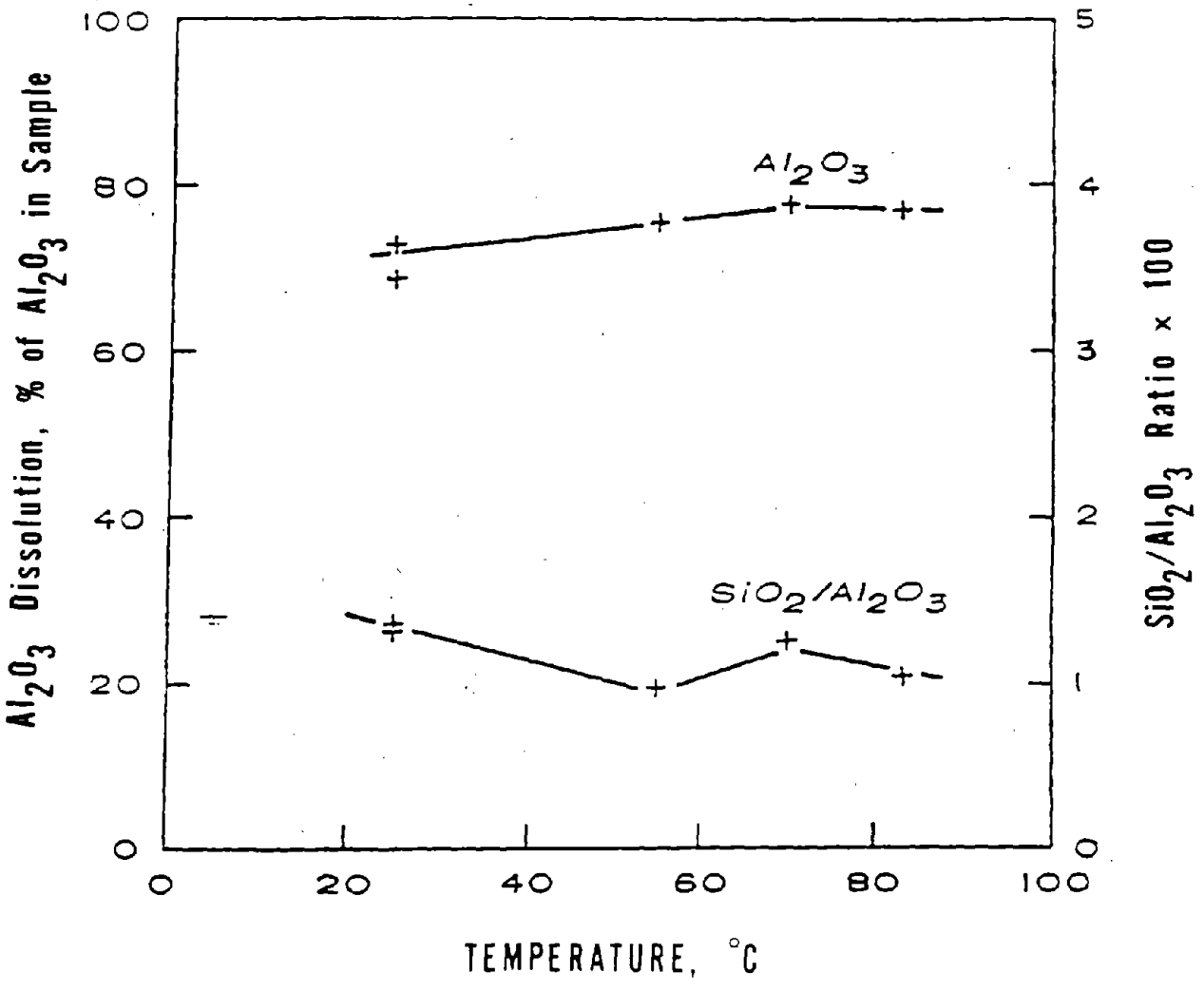

Fig. 4. Effect of temperature on Al_2O_3 and SiO_2 dissolution in 5.6 g/ℓ NaOH solution: solid/liquid ratio = 0.2; leaching time = 40 minutes.

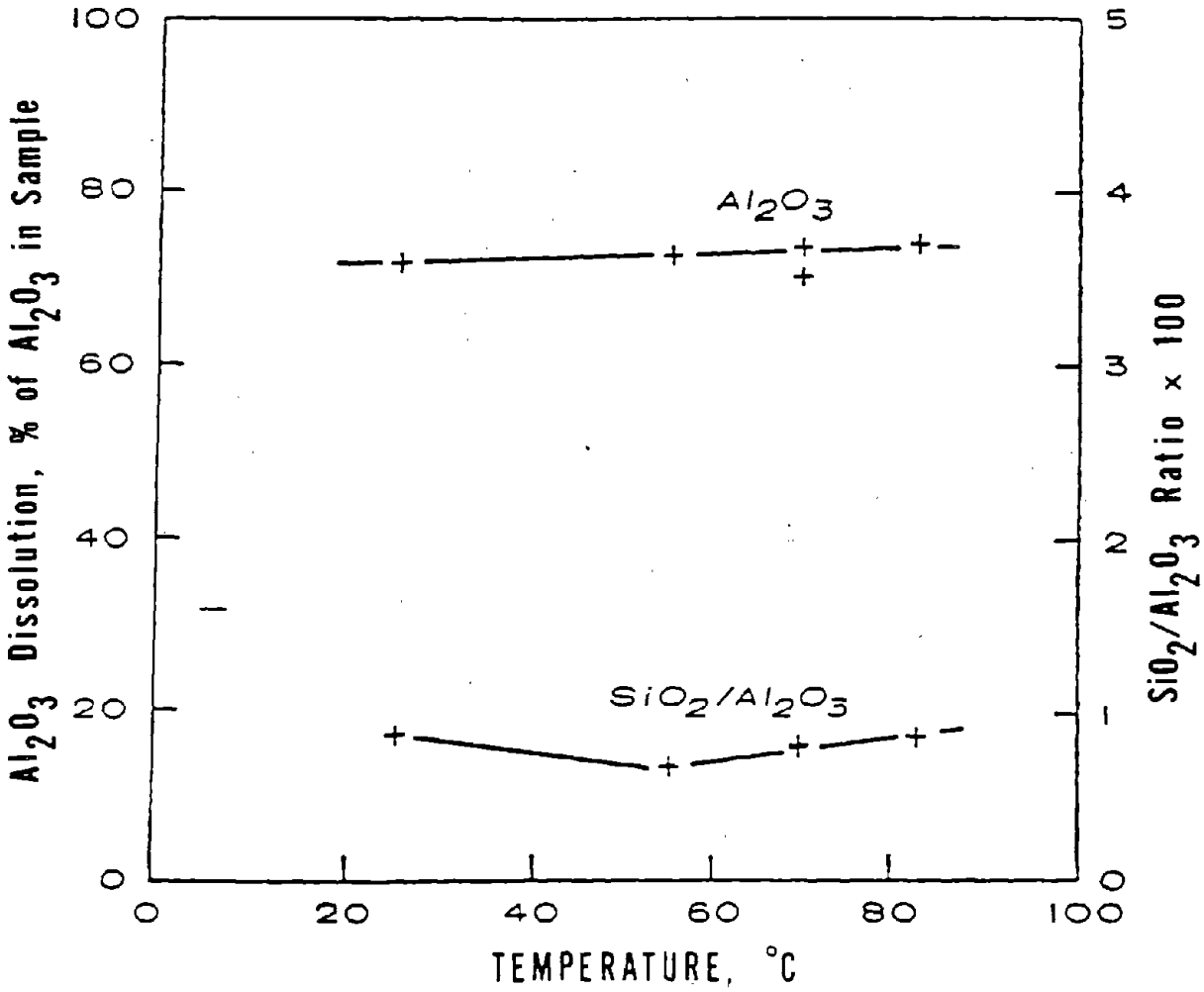

Fig. 5. Effect of temperature on Al_2O_3 and SiO_2 dissolution in water: solid/liquid ratio = 0.2; leaching time = 40 minutes.

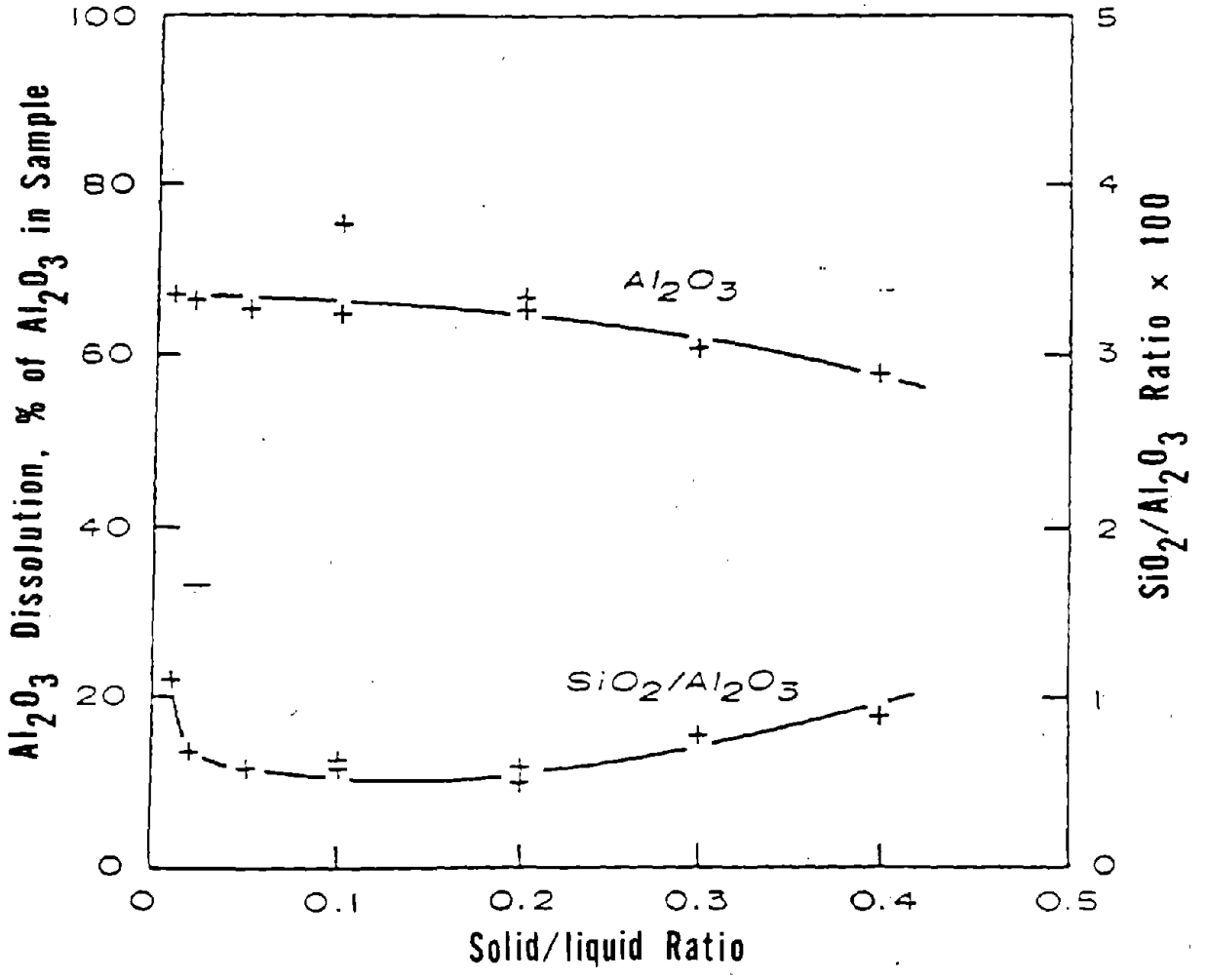

Fig. 6. Dissolution of Al_2O_3 and SiO_2 vs. solid/liquid ratio in water leaching of sinters at 70°C for 40 minutes.

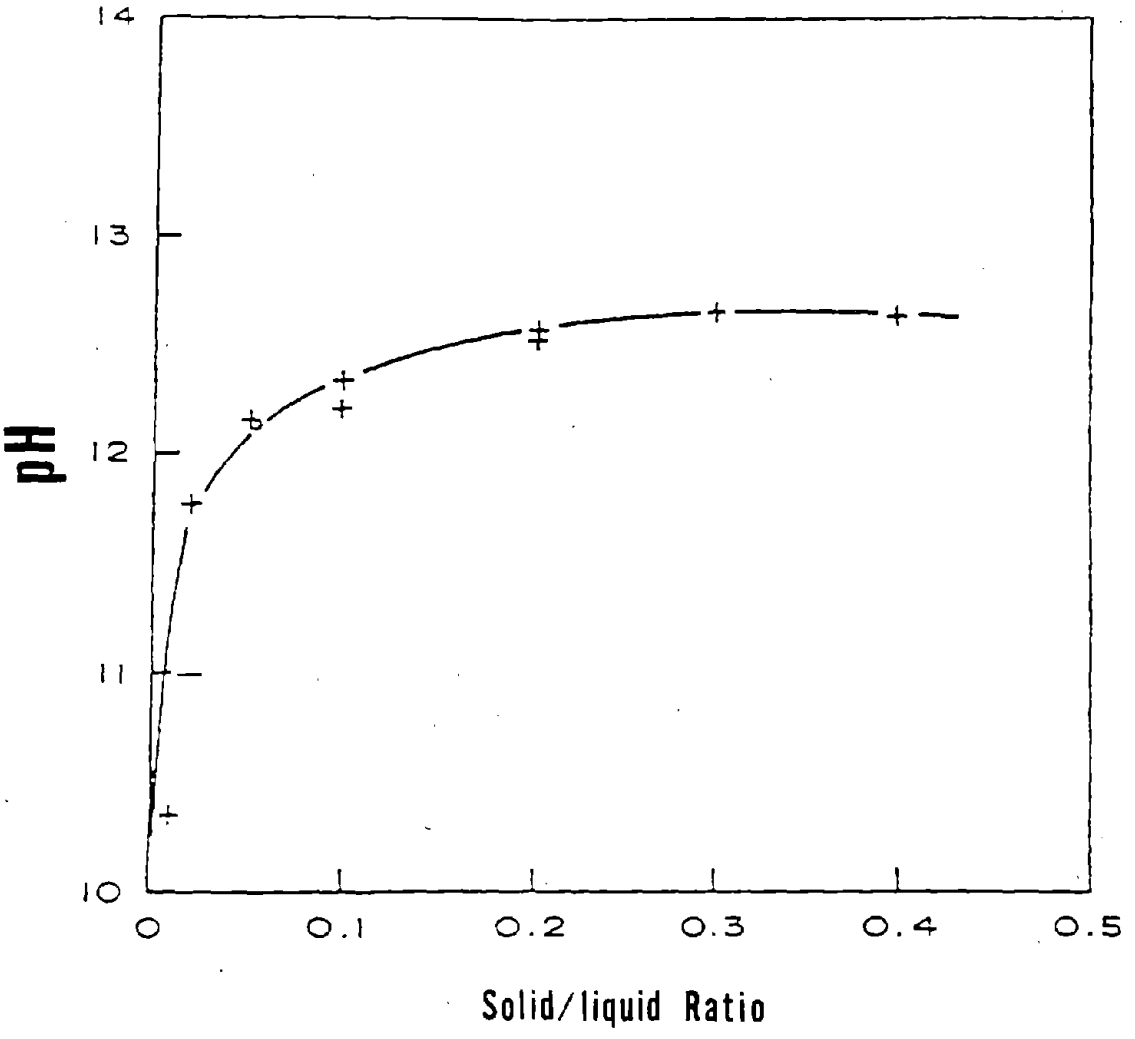

Fig. 7. pH variation of the pregnant solution with change in solid/liquid ratio.

The dissolution of sodium aluminate in water is believed to proceed according to (10):

$$NaAlO_2 + 2H_2O = Al(OH)_4^- + Na^+ \quad (1)$$

$$Al(OH)_4^- = Al(OH)_3 + OH^- \quad (2)$$

Therefore, the stability of aluminate ion is possible only in the presence of excess OH^- ions.

In general, the use of Na_2CO_3 and NaOH solutions as the extracting media is more beneficial to sinters with relatively low extraction characteristics (such as the calcium aluminates from the lime sinter process) than to sinters that exhibit good extraction in water. Additional Na_2CO_3 in leaching was also used for the purpose of increasing the stability of the sodium aluminate liquor (8). During this study, the water-leached sodium aluminate solution was stable for at least 24 hours.

Gelation in the leaching stage was always considered in previous lime-soda sinter studies as potentially the most serious technical problem. The symptoms of gelation such as swelling and thickening of the slurry were not observed in this study. Only normal compaction due to settling occurred. The slurries were easily repulped by agitation even after periods as long as 72 hours. However, precipitation and crystal growth started after this time.

Desilication

In the leaching study, emphasis was placed on the maximum extraction of alumina from the coal-waste sinter. As a result, the pregnant liquor contained silica. Then, the problem was the removal of silica from the liquor before the precipitation of alumina.

The composition of the pregnant liquor subjected to desilication was 12-15 g/l Al_2O_3 and 0.08-0.25 g/l SiO_2. These concentrations correspond to s/l ratio = 0.2 which was found to give the lowest SiO_2 content in the solution as shown previously.

Figure 8 shows the effect of $Ca(OH)_2$ suspension (10 g/l $Ca(OH)_2$) on the

desilication process during the heating of sodium aluminate solution from 25°C to boiling point in 60-minute periods. Silica concentration in the pregnant liquor drops sharply with an increase in $Ca(OH)_2$ addition up to 0.2 liter per liter of pregnant liquor. Alumina content also decreases gradually with the increase of $Ca(OH)_2$ addition. Therefore, the mass corresponding to 0.2 liter of $Ca(OH)_2$ suspension per liter of pregnant liquor is the optimum amount to render high desilication with low alumina losses.

The effect of time on desilication can be seen in Figure 9. This figure shows that desilication is rapid. At about 5 minutes the desilication curve reaches the equilibrium concentration at room temperature.

Temperature has an interesting effect on silica removal as seen in Figure 10. The silica content of sodium aluminate solution increases with increasing temperature. This effect is the opposite of the literature data (5,8,10). This phenomenon could be due to the difference in the composition of the pregnant liquor of this study from the earlier investigation, the main difference being the content of carbonate ions in the liquors used in the past. It was found experimentally that an equilibrium exists between the carbonate ion concentration and caustic alkalinity of the solution (9). This equilibrium is important for the formation of hydrated calcium aluminates needed for desilication.

In the $CaO-Al_2O_3-H_2O$ system, it is known that at 25°C the solid phases having true solubility curves are bivsite ($Al(OH)_3$), cubic tricalcium aluminate hexahydrate ($3CaO\cdot Al_2O_3\cdot 6H_2O$), and calcium hydroxide ($Ca(OH)_2$). During desilication, $Ca(OH)_2$ reacts with $Al(OH)_4^-$ to form $3CaO\cdot Al_2O_3\cdot 6H_2O$ and metastable compounds; below 100°C the metastable hexagonal calcium-aluminate hydrates react with the solution to form the final stable tricalcium aluminate hexahydrate. Therefore, in the process of thorough desilication, the following reaction proceeds (9):

$$3Ca^{2+} + 2Al(OH)_4^- + 4OH^- = 3CaO\cdot Al_2O_3\cdot 6H_2O \qquad (3)$$

The product of reaction (3) reacts with the silicate ions via heterogeneous reaction on the surface of the precipitate formed to produce a hydrated Ca-Al-Si-O compound:

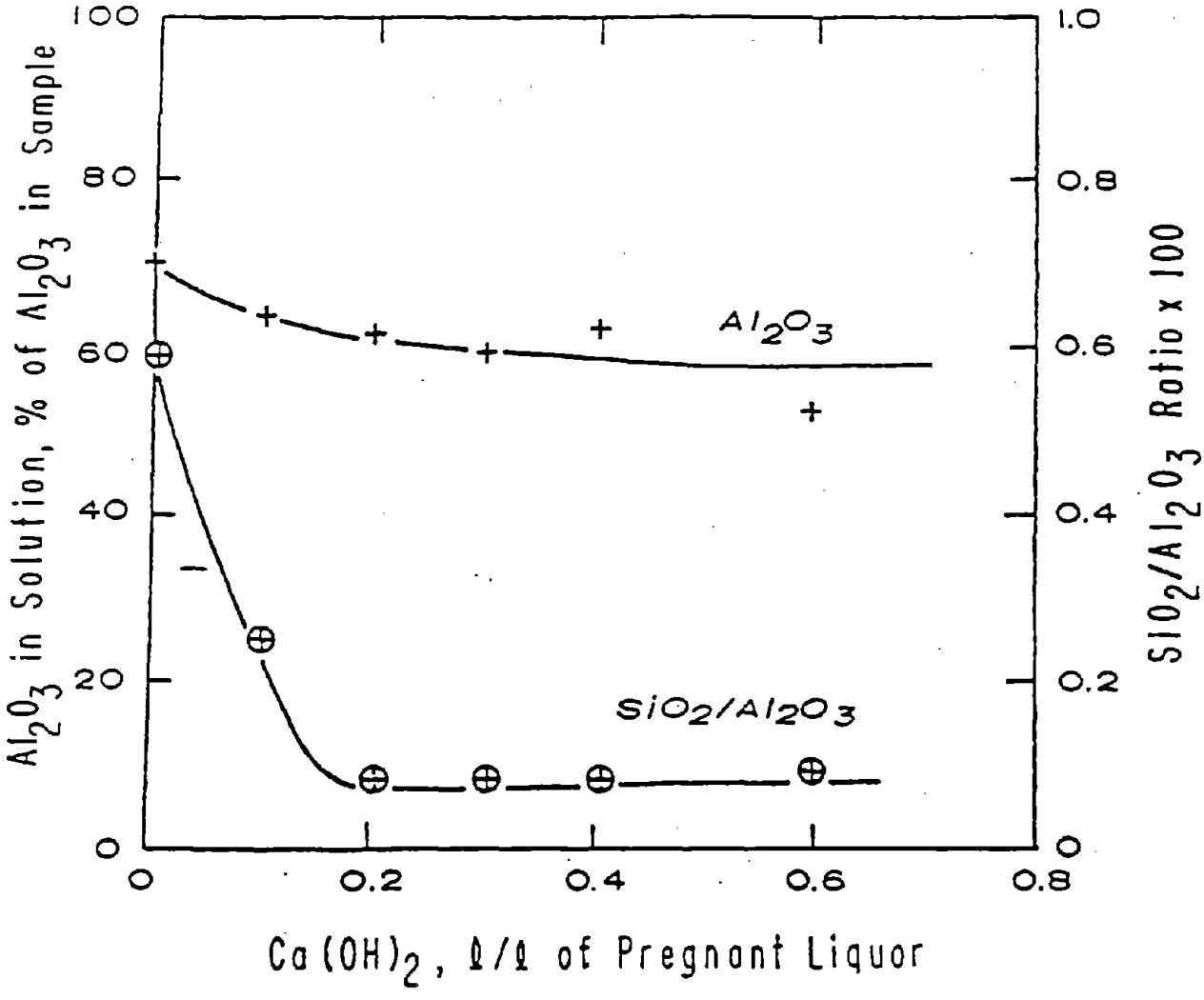

Fig.8: Effect of $Ca(OH)_2$ addition (10 g/ℓ $Ca(OH)_2$ suspension in water) on desilication of sodium aluminate during heating from 25^{o} to $95^{o}C$.

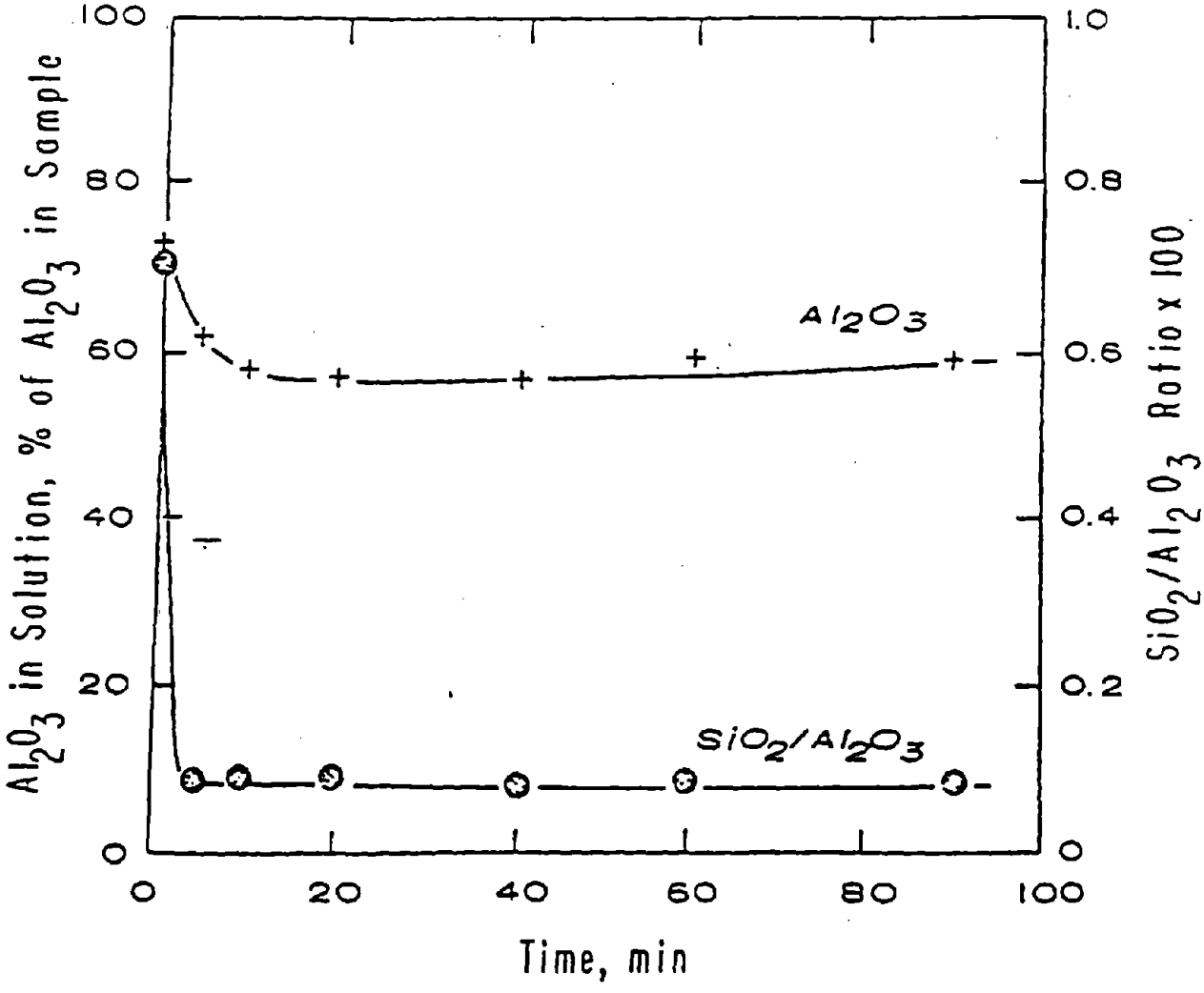

Fig.9: Desilication of sodium aluminate solution with $Ca(OH)_2$ suspension at 25°C.

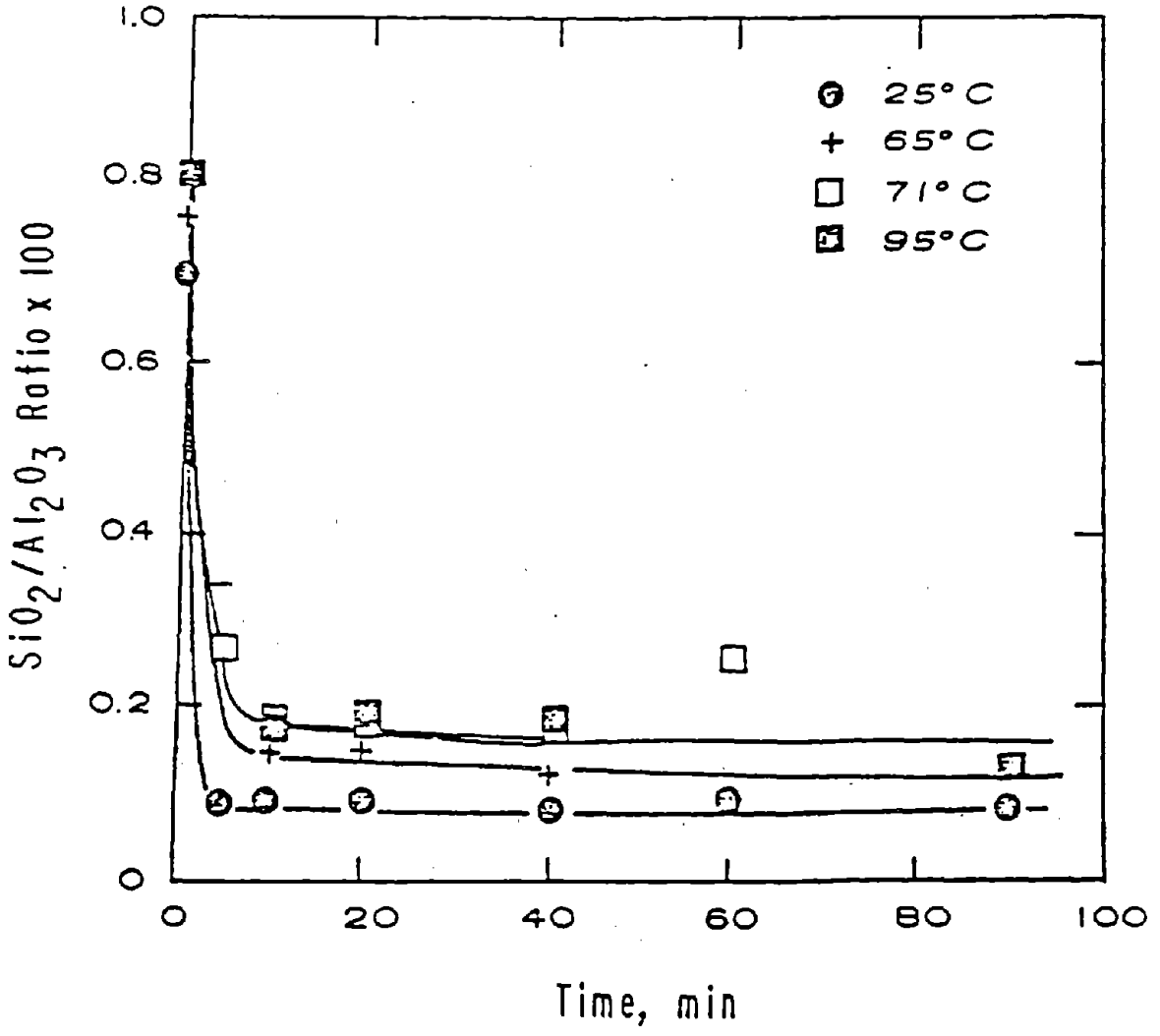

Fig.10: Effect of temperature on desilication of sodium aluminate solution with $Ca(OH)_2$ suspension.

$$3CaO\cdot Al_2O_3\cdot 6H_2O + xSiO_3^{2-} = 3CaO\cdot Al_2O_3\cdot xSiO_2\cdot (6-x)H_2O + 2x(OH)^- \quad (4)$$

where x depends on the method used for obtaining tricalcium aluminate (9).

When reaction (4) occurs, the content of caustic alkali in the solution increases and that of the alumina decreases. As a result of reaction (4), the stability of the sodium aluminate varies, too. Losses in alumina during desilication occur via reactions (3) and (4). This is shown mainly in Figure 8 where the decrease of alumina content in the solution is seen to depend on the mass of $Ca(OH)_2$ added to the solution.

The decreasing solubility of $Ca(OH)_2$ with increasing temperature at atmospheric pressure (11) would account in part for the lower desilication at high temperatures.

Carbonation and Alumina Recovery

The desilicated sodium aluminate solution was treated with CO_2 gas. The precipitate, after filtration, was subjected to calcination. The principal chemical reaction that occurs during carbonation is as follows:

$$2OH^- + CO_2 = CO_3^{2-} + H_2O \quad (5)$$

When this reaction sufficiently decreases the $(OH)^-$ concentration of the solution, the aluminate ion decomposes according to reaction (2).

X-ray diffraction analysis of the dried precipitate obtained from desilicated sodium aluminate solution showed that the precipitate was amorphous material with poorly crystallized alumina monohydrate. The x-ray diffraction pattern of the precipitate calcined at 1250°C showed only α - alumina peaks, as seen in Figure 11.

Analysis of the solution at this stage showed that, for a 97% alumina precipitation from solution containing 0.056% silica (dry alumina basis), 20% of this silica precipitated. Therefore, the alumina precipitate contained 0.011% SiO_2. The amount of precipitated silica in carbonation depends upon the concentration of silica in the liquor and upon the amount of alumina precipitation; consequently, control of these two parameters should yield

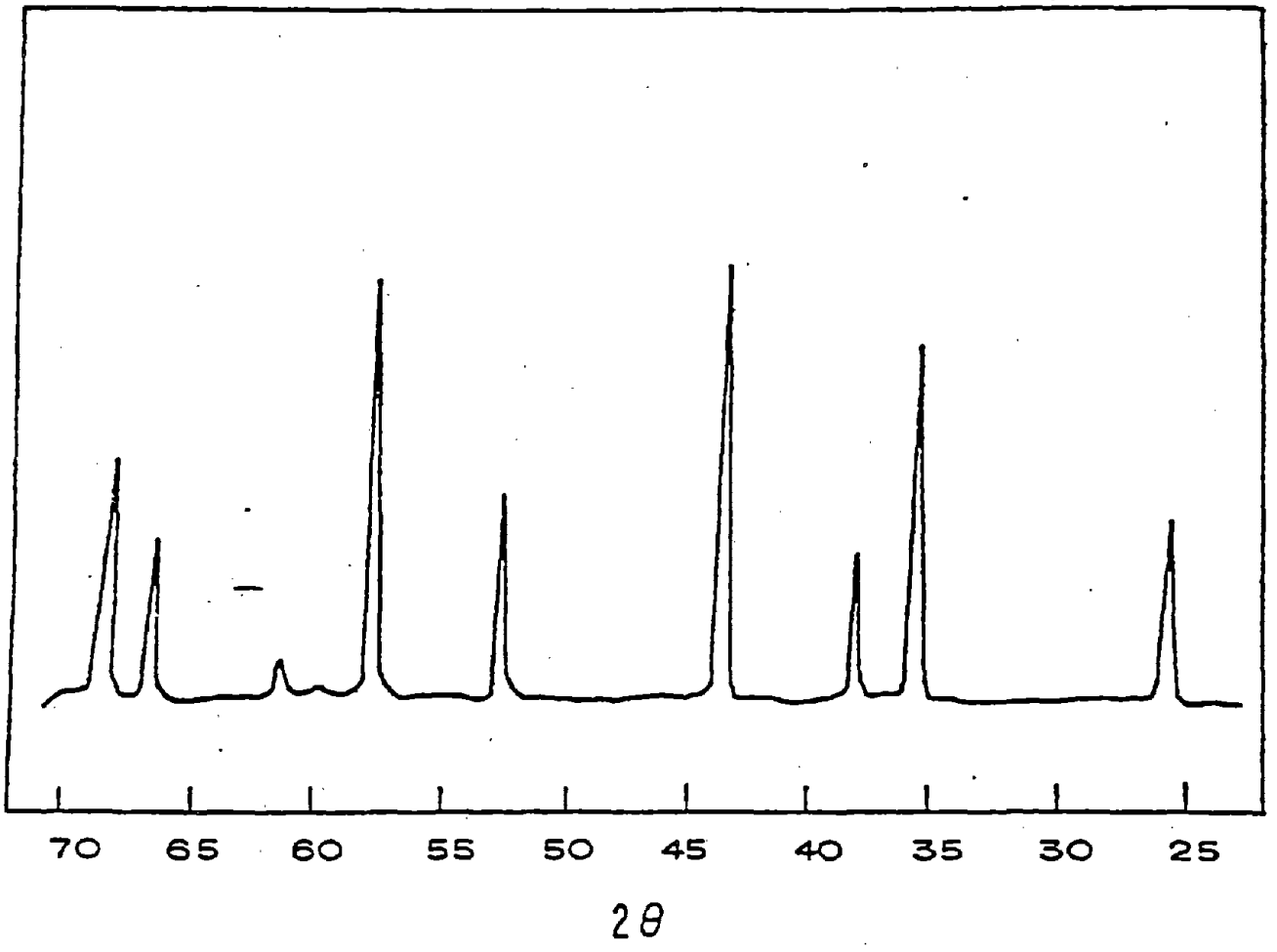

Fig. 11. X-ray diffraction pattern of the calcined precipitate (at 1250°C) matching perfectly with the d dimension of α-alumina.

high-purity alumina with the silica content below the maximum level for electrolytic reduction of alumina given as 0.012-0.020% SiO_2 (12).

CONCLUSIONS

From the study of the different variables involved in leaching of coal-waste sinters and desilication of the aluminate liquor, the following conclusions can be drawn:

The coal-waste sinters exhibit good alumina extraction characteristics in water leach with the lowest silica content of the liquor compared to leaching with NaOH and Na_2CO_3 for an s/l ratio of 0.2 at low temperatures. Under these conditions, gelation of the slurry does not occur, and stable aluminate solutions are obtained.

The sodium aluminate liquor from water leach readily responds to desilication with $Ca(OH)_2$ at room temperature and atmospheric pressure.

Alumina with silica content below the reduction-grade level can be produced by carbonation of the purified aluminate solution followed by calcination.

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Chapter 2

ALUMINA FROM COAL WASTES BY CARBOTHERMAL REDUCTION IN THE PRESENCE OF NITROGEN

INTRODUCTION

Currently, the Bayer process accounts for virtually all of the alumina production in the world. This process depends on bauxite ore, which is in short supply in the United States. In fact, the U.S. imports more than 90% of the approximately 3,500,000 tons per year of the bauxite it uses. To avoid becoming dependent on foreign imports, the U.S. is seeking alternative resources and technologies. Many other aluminum-bearing minerals besides bauxite are abundant. Several innovative processes using non-bauxite domestic raw materials have been analyzed and reviewed under a U.S. Bureau of Mines contract (1).

A process using coal-waste material to produce alumina has been investigated in this work. This is attractive in that a waste containing 10-30% Al_2O_3 and 20-70% SiO_2 that normally must be discarded can be used as a resource. The carbon inherently present in the waste helps reduce the alumina under a nitrogen atmosphere to form aluminum nitride and silicon carbide according to the following reactions:

$$Al_2O_3 + 3C + N_2 = 2AlN + 3CO \qquad (1)$$

$$SiO_2 + 3C = SiC + 2CO \qquad (2)$$

With carbon alone, the reduction of alumina is very difficult and a high temperature is required (2). However, in a nitrogen atmosphere, alumina can be reduced to aluminum nitride, a reaction possible at a lower temperature.

The aluminum nitride is leached in a caustic solution to form sodium aluminate, which can subsequently be treated to produce aluminum hydroxide or alumina. As seen in reactions (2) and (3), two valuable by-products, silicon carbide and ammonia, are obtained:

$$AlN + NaOH + H_2O = NaAlO_2 + NH_3 \qquad (3)$$

The basic reaction scheme was originally patented by Serpek (2) using bauxite ore. Recently, Cutler (4) proposed applying the process to clay. Because clay is a component of coal wastes, the process is considered to be applicable

to these wastes. The fuel value in the coal is expected to supply some of the energy requirements.

EXPERIMENTAL

Coal waste in the form of preparation plant material was obtained from a New Mexico strip mine. It was reduced in size by standard processing techniques. By the use of atomic absorption spectroscopy and x-ray flourescence, the alumina and silica contents were determined to be 18.0 and 52.6%, respectively. A mineralogical analysis showed the primary constitutents to be quartz and kaolinite mixed with minor amounts of other aluminosilicates.

A closed-system vertical furnace capable of reaching a temperature of 1700^{o}C was used. Samples were suspended in the furnace and held for the required reaction time.

A leaching system was constructed consisting of a stirring hot-plate, Teflon beaker and a condensation tube. Teflon was used because caustic solutions at high temperatures leach silica from glassware. Silica is an impurity in the system and should be avoided.

Sample analysis was done by x-ray diffraction using a Norelco diffractometer and Cu-K alpha radiation.

RESULTS

As given by equations (1) - (3), the reactions to obtain alumina from coal wastes appear relatively simple. However, the impurities in the waste and various possible side reactions complicate the process. When the coal waste material in its original form was reacted under a nitrogen atmosphere at 1450^{o}C, x-ray diffraction analysis showed that mullite as well as silicon carbide was formed. Aluminum nitride was not present. The waste contains 14% carbon. This is less than stoichiometrically needed for completion of reactions (1) and (2). Excess carbon in the form of carbon black was added to assure complete reaction.

With 10% excess carbon and a temperature of 1450^{o}C, x-ray diffraction analysis showed the major products of the reaction to be aluminum nitride,

beta-silicon carbide, and beta silicon nitride. Some minor constituents such as ferrosilicon and alpha-silicon nitride were also identified. The impurities in the waste must also exist in some form in the final product. However, x-ray cannot detect such small quantities.

X-ray diffraction is adaptable to quantitative analysis through the use of correction factors. For this study, relatively pure samples of aluminum nitride, silicon nitride and silicon carbide were obtained. Different proportions of these three were mixed and analyzed using x-ray. The heights of specified intensity peaks as the diffraction patterns were measured and compared. Standard calibration curves as shown in Figure 1 comparing the ratio of the peak heights were developed. From these standards the relative amounts of aluminum nitride, silicon carbide and silicon nitride found in the experiments were determined. Hoggard (5) used a similar technique in determining alumina content in SIALON. This provides a quick method (with accuracy rivaling that of a chemical analysis) to determine relative amounts of products without having to perform a chemical analysis on every product.

Experiments showed that as the reaction proceeds, the amount of silicon carbide formed decreases while the amounts of silicon nitride and aluminum nitride formed increase. A typical example is shown in Figure 2. Lee (6) observed a similar occurrance with regards to silicon carbide in his study on the carbothermal reduction. He saw two distinct stages in the reaction of silica being reduced with carbon. The reaction proceeded rapidly to about 30% conversion and then tapered off considerably. This suggested that silicon carbide formed in the first stage followed by the slower reduction of silica by silicon carbide in the second.

$$SiO_2 + 3C = SiC + 2CO \qquad (2)$$

$$\underline{2SiO_2 + SiC = 3SiO + CO} \qquad (4)$$

$$SiO_2 + C = SiO + CO \qquad (5)$$

Other researchers have made similar observations (7-10). It is further postulated that the SiO gas produced reacts with nitrogen to form silicon nitride.

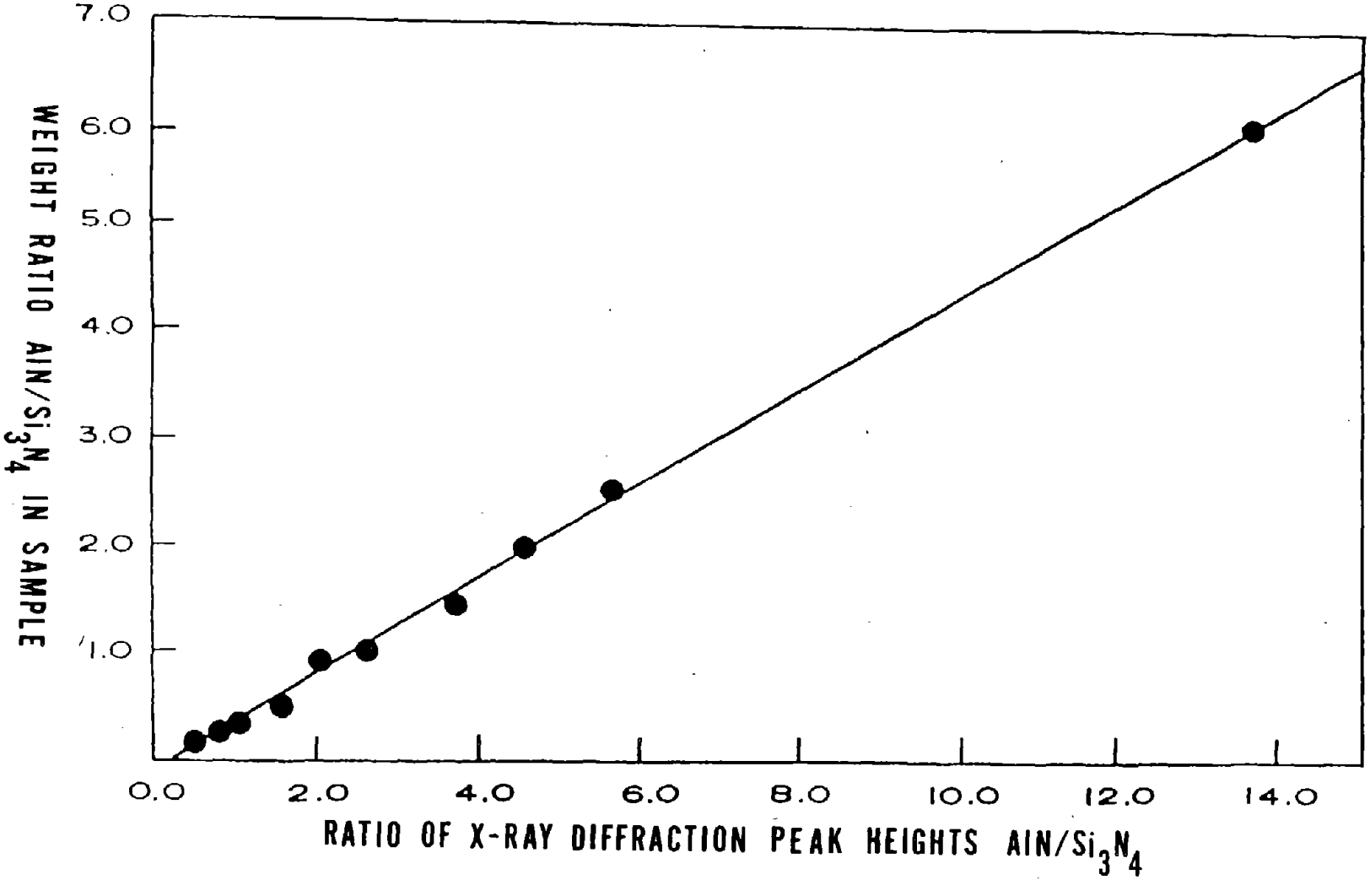

Fig. 1. X-ray diffraction calibration curve used for quantitative analysis of reaction products.

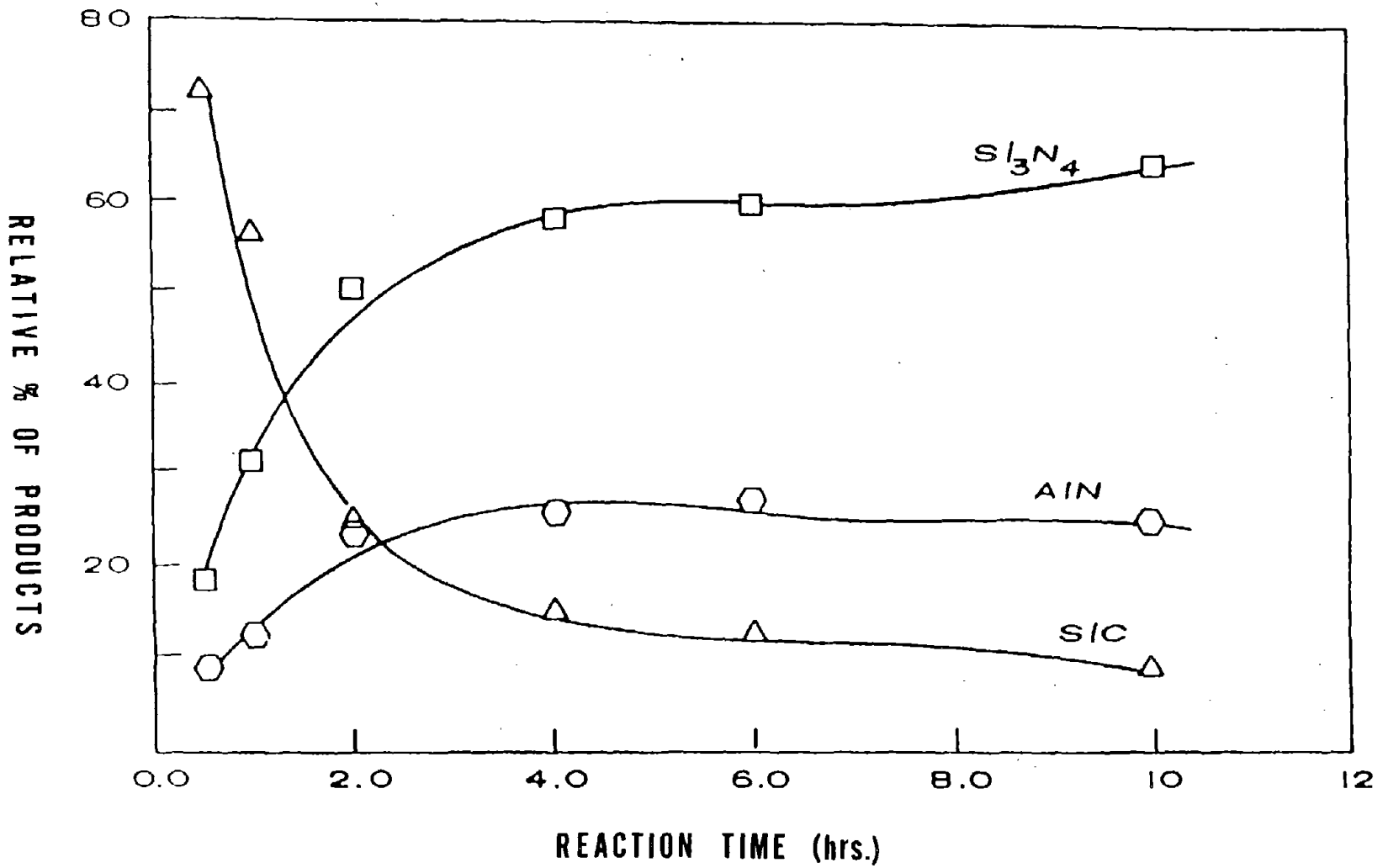

Fig. 2. Formation of compounds at 1450°C (10% excess carbon).

$$SiO + 2/3N_2 + C = 1/3Si_3N_4 + CO \qquad (6)$$

This mechanism would account for the increase in the formation of silicon nitride.

To examine the effect of excess carbon, a set of samples was prepared with varying amounts of excess carbon mixed with the coal waste. Each was reacted for two hours at 1500°C under a nitrogen atmosphere. The results are given in Table I. As the amount of carbon increases, so does the amount of silicon carbide formed, while the amount of aluminum nitride and silicon nitride formed decreases. An excess of carbon seems to hinder the production of aluminum nitride and silicon nitride. With excess carbon, conditions remain favorable for free silica to react more completely. Consequently, the reduction of the alumina in the aluminosilicate material to aluminum nitride is delayed. However, it is expected that the conversion to aluminum nitride will go to completion if the reaction time is increased.

Table I. Effect of Excess Carbon*

Percent Excess Carbon**	Percentage of Products***			Percent Conversion****		
	AlN	SiC	Si_3N_4	AlN	SiC	Si_3N_4
10	33.8	16.9	49.3	99.0	19.7	66.6
20	31.2	22.0	46.8	93.7	25.6	63.2
50	15.8	74.0	10.3	47.4	87.2	11.9
100	11.4	86.6	2.0	34.2	98.0	1.9

* Reaction at 1500°C for 2 hours.

** % of original coal waste.

*** Impurities excluded to make total of AlN + SiC + Si_3N_4 = 100%.

**** Percent of original amount in coal waste converted to product.

A large surface area maximizes the sites available for gaseous reactions to occur and thereby increases the reaction rate. To test this assumption, experiments were performed varying the particle size of the wastes. The

carbon black was maintained at -200 mesh. Four different size fractions of wastes were used: -200, -100+200, -65+100 and -48+65 mesh. Table II lists the results. As the particle size increases, the formation of aluminum nitride and silicon nitride decreases. The reaction rate decreases with increasing particle size, as is consistent with the proposed mechanism.

Thermodynamic calculations of the reactions involved show them to be endothermic. Since heat is required for the reaction to proceed, raising the temperature should favor the reaction. Experiments were run at as low as

Table II. Effect of Particle Size*

Particle Size (mesh)	Relative Percent of Products**			Percent Conversion***		
	AlN	SiC	Si_3N_4	AlN	SiC	Si_3N_4
-200	30.7	23.6	45.7	92.2	27.4	61.8
-100+200	24.3	23.2	52.6	73.0	27.0	71.1
-65+100	21.7	30.1	48.2	65.2	35.0	64.9
-48+65	21.4	36.9	41.7	64.3	42.9	56.4

* Reaction of 1500°C for 2 hours; 10% excess carbon.

** Impurities excluded to make total of AlN + SiC + Si_3N_4 = 100%.

*** Percent of original amount in coal waste converted to product.

1300°C. No aluminum nitride formed, but silicon carbide and silicon nitride were detected. When the temperature was increased to 1350°C, aluminum nitride formed. This temperature is somewhat lower than other investigators claim is necessary for this reaction.

As indicated in Table III, increasing the temperature enhances the formation of aluminum nitride to some degree. The optimal temperature range is approximately 1450-1500°C for 1.5 to 3 hours reaction time. At these conditions, roughly 95% of the alumina originally present in the coal waste is converted to aluminum nitride. However, if the temperature is too high or the reaction time too long, the amount of aluminum nitride detected drops off. In an article, reviewing the Serpek process (11), it was noted that overheating causes the material to fuse together, thus destroying porosity and causing nitrification to cease. A more recent patent (12) states that in the alumina-

Table III. Effect of Temperature*

Time (hours)	Temperature (°C)	Relative Percent of Products**			Percent Conversion***		
		AlN	SiC	Si_3N_4	AlN	SiC	Si_3N_4
1	1500	15.3	52.6	32.1	45.9	61.2	43.4
	1550	18.7	58.4	22.9	56.1	67.9	30.9
	1600	29.6	22.5	47.9	88.9	26.2	64.7
2	1350	27.4	44.9	27.7	82.2	52.2	37.4
	1450	32.7	46.8	20.5	98.2	54.4	27.7
	1500	30.5	19.1	50.4	91.6	22.2	68.1
	1550	29.2	26.8	44.0	87.7	31.2	59.5
3	1400	21.0	31.4	47.6	63.0	36.5	64.3
	1500	30.1	13.0	56.1	90.4	15.1	76.9
	1550	24.0	17.8	58.2	72.0	20.7	78.6
4	1400	27.5	31.2	41.3	82.6	36.3	55.8
	1450	30.1	35.3	34.6	90.4	41.0	46.8
	1500	27.6	14.2	58.2	82.9	16.5	78.6
	1550	21.8	10.3	67.9	65.5	12.0	86.8
6	1350	25.7	11.2	63.1	77.2	13.0	85.3
	1400	24.7	27.4	47.9	74.2	31.9	64.7
	1450	30.8	44.0	25.2	92.5	51.2	34.1
10	1350	26.5	9.3	64.2	79.6	10.8	86.8
	1450	30.9	22.8	46.3	92.8	26.5	62.6

* 10% excess carbon.

** Impurities excluded to make total of AlN + SiC + Si_3N_4 = 100%.

*** Percent of original amount in coal waste converted to product.

nitrogen-carbon system, overheating of the reactants involves volatilization which may cause sintering, thus impairing the quality of the end product. Because of the complexity of the system, other compounds could be forming, causing decreased production of aluminum nitride.

Several of the experiments in this study were completed using pelletized reactants, formed in a hydraulic press with a suitable die. For the lower temperatures 1400-1450°C, pelletizing enhanced the reaction. At 1500°C pelletizing the sample caused the end product to partially sinter. The longer the pellet was reacted, the more difficult it became to remove, analyze and

leach. Therefore, pelletizing is not recommended.

In separate experiments it was found that the rate of nitrogen gas flow appears to have only a slight effect on the final products. However, lack of nitrogen brings about partial sintering of the charge which makes completion of the nitriding operation impossible (12). Therefore, nitrogen must be constantly flowing.

The success of this process rests on the ability to leach the aluminum nitride to obtain alumina and ammonia. Several leaching experiments were performed on products of reaction obtained at 1500°C for two hours reaction time to obtain the optimal leaching conditions. It was found that the best recovery occurred after two hours leaching time in a one-mole concentration of sodium hydroxide at the boiling temperature. As seen in Figure 3, the recovery of alumina from aluminum nitride goes through a maximum as the reaction time at high temperature increases. This confirms the assumption that the leachable amount of aluminum nitride formed decreases with increasing reaction time. Beyond 1.5 to 3 hours in the furnace the recovery of alumina by leaching decreases significantly. At these lengths of time the aluminum nitride produced is not readily leached.

In the 1920's, Alcoa (2) performed extensive leaching experiments on aluminum nitride produced by reaction (1). Because of the refractory behavior of the nitride, many difficulties were encountered. Studies showed that the crystalline variety of aluminum nitride formed at these high temperatures was much more difficult to decompose than anticipated. In 1956, Kohn et al. (13) obtained small crystals of AlN while working at high temperatures on another project. Analysis showed that the crystals were relatively inert. A few years later, Long and Foster (14) produced high-purity AlN by striking a d.c. arc between two high-purity aluminum electrodes in a nitrogen atmosphere. They found an extreme chemical inertness of the AlN formed at these very high temperatures. These and other findings led Taylor and Lenie (15) to conclude that AlN prepared at high temperatures is relatively inert.

In this study, some of the aluminum nitride obtained was heated at 1500°C for two hours under a nitrogen atmosphere. Leached under optimal conditions, only 85% of the alumina was recovered, verifying the above assumptions.

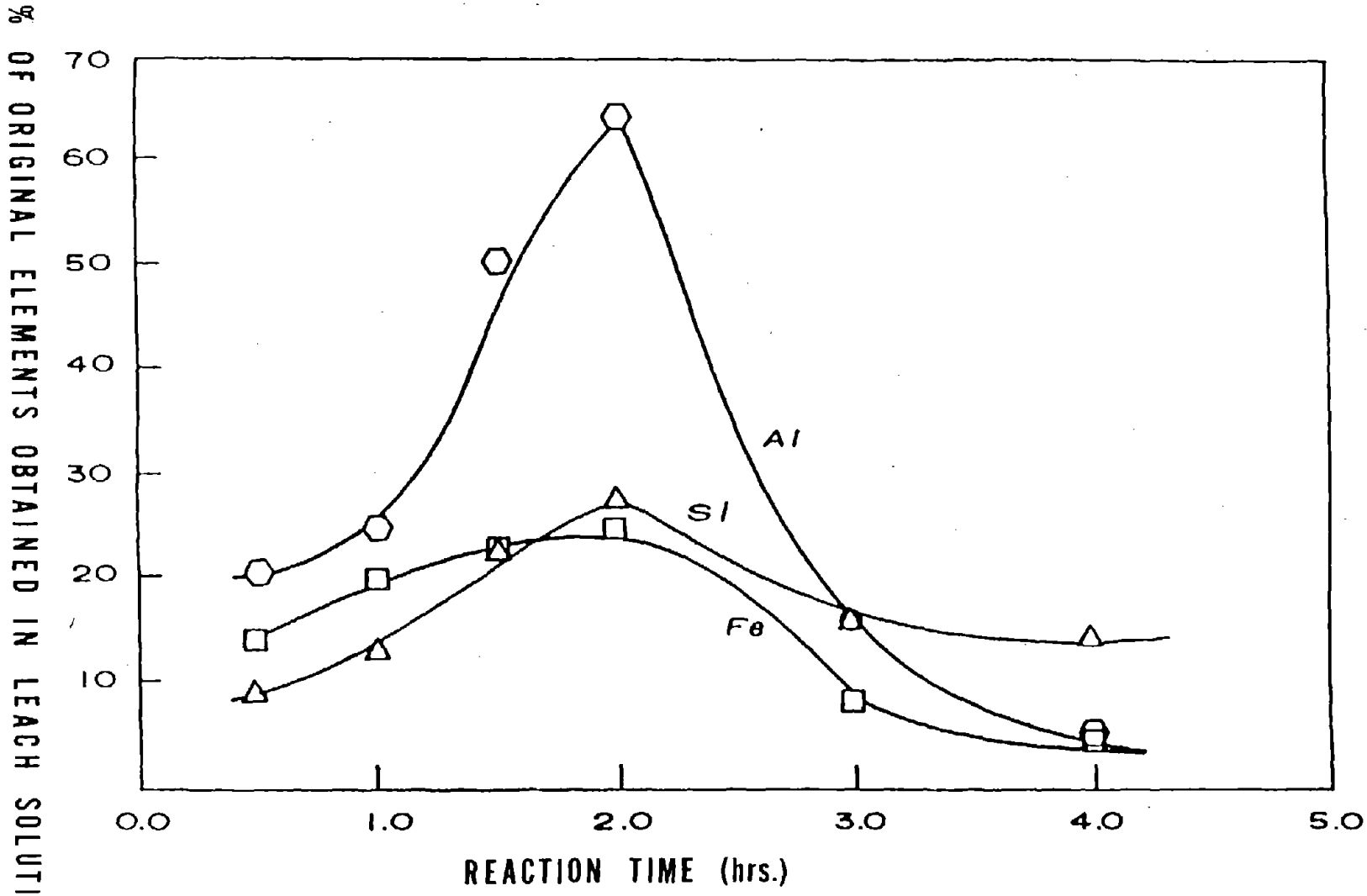

Fig. 3. Leaching of reaction products obtained at 1550°C.

Once AlN is digested, a pure form of alumina must be precipitated. Iron and silica impurities must be removed before alumina can be precipitated. Removal of iron proved to be relatively easy because it drops out of solution before silica or alumina. Silica is more difficult to remove. The traditional Bayer method of desilication proved ineffective in this system. A method proposed by Noworyta (16) gave promising results. In this procedure the pH of the solution is adjusted to 12.5 with the aid of hydrochloric acid. Next, the temperature is raised to 96^{o}C. A given amount of a 10 g/l solution of calcium hydroxide was added and the entire solution was left to desilicate for one hour. Figure 4 shows that almost all of the silica can be removed as calcium aluminosilicate with most of the alumina remaining in solution. Approximately 10% of the alumina is lost to the calcium aluminosilicate. If too much calcium hydroxide is added, alumina can be totally precipitated out of solution. Care must be taken to add the correct amount of desilicant.

With iron and silica removed, alumina was precipitated by bubbling carbon dioxide gas through the alumina-rich solution according to the following reaction:

$$2NaAlO_2 + CO_2 + 3H_2O = Al_2O_3 \cdot 3H_2O + Na_2CO_3 \qquad (7)$$

This precipitate was washed with warm water to dissolve any precipitated salts and calcined in a platinum crucible at a temperature at 1200^{o}C to remove the waters of hydration.

$$Al_2O_3 \cdot 3H_2O = Al_2O_3 + 3H_2O \qquad (8)$$

X-ray diffraction analysis showed alumina to be the final product. Any aluminum hydroxide not precipitated can be recycled and allowed to precipitate again.

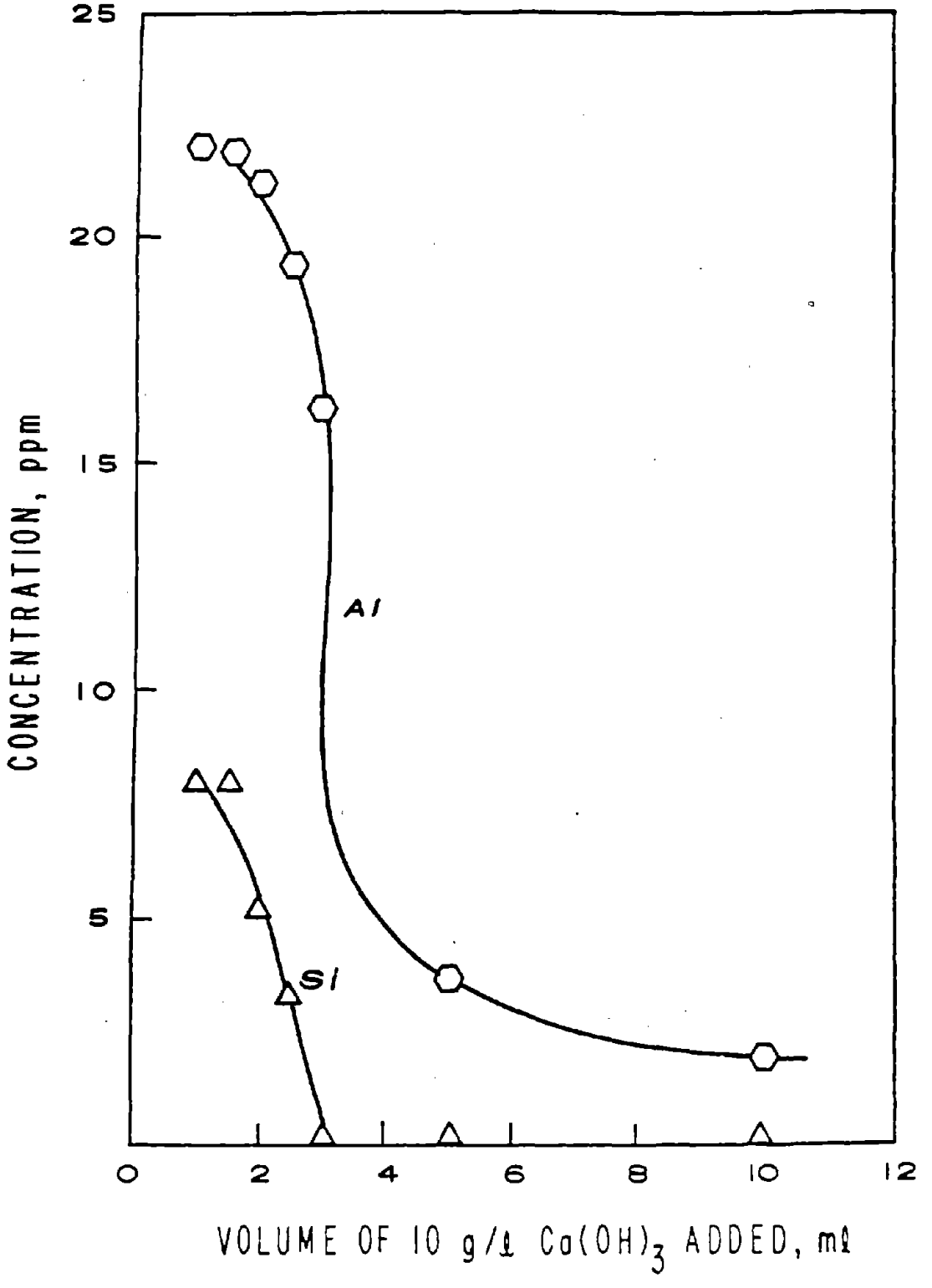

Fig. 4. Desilication of sodium aluminate solution.

CONCLUSIONS

An alternative to the Bayer process for obtaining alumina was investigated in this study. The process consists of three basic stages, each of which was investigated to obtain optimal operating conditions for the highest yield of alumina. If each stage is operated at optimum conditions, then the overall conversion of alumina from the coal waste is approximately 60%. The leaching of aluminum nitride from the high-temperature reaction mixture presents the step with the lowest recovery. Further work is necessary to improve the efficiency of this step.

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Chapter 3

SEPARATION OF ALUMINA BY THE VOLATILIZATION OF SILICA

INTRODUCTION

The carbothermal reaction between carbon and coal wastes under argon atmosphere is a direct method to produce valuable materials such as alumina and silicon carbide. Compared to other extraction processes from clay or fly ash, a higher temperature is required. But this carbothermal process has the advantages of obtaining silicon carbide as a by-product. Since coal waste is intimately mixed with carbon, this carbon is used as a fuel as well as a reducing agent. The Gibbs energy data for possible reactions in this system reveal that high temperature is required for the volatilization of silica as shown in Figure 1 (1) . However, as the product CO gas is purged with an argon gas flow and the activity of silica in aluminosilicates can be less than one, the carbothermal reduction can be carried out at a temperature which is much lower than the equilibrium temperature involving reactants in pure states. Due to the impurities contained in coal waste it is essential that the product of the carbothermal reduction should be purified to obtain pure alumina. First, the silicon carbide is separated from alumina and then the other impurities remaining in the product must be removed.

EXPERIMENTAL PROCEDURE AND RESULTS

1. Sample Preparation:

For the solid-solid reaction taking place initially, the surface area of reactant is very important. Moreover, CaO in the original coal wastes reacts with alumina and forms $6Al_2O_3 \cdot CaO$ as the carbothermal reaction proceeds. Therefore, CaO must be removed before the reduction.

Accordingly, coal wastes were ground and then treated with 0.5 M HCl at 60^oC for 2 hours. Pretreated sample was dried, sieved (-270+400 mesh), and well mixed with very fine carbon black (-400 mesh).

Pelletizing the coal waste/carbon reactants was found to be useful in that it helps the separation of the product and prevents the loss of the sample because of gas blowing. So the mixture of the sample is made into small pellets (4 to 12 mm in diameter) under 5,000 psi. The analysis of pretreated coal wastes is shown in Table I compared with the original sample (2) .

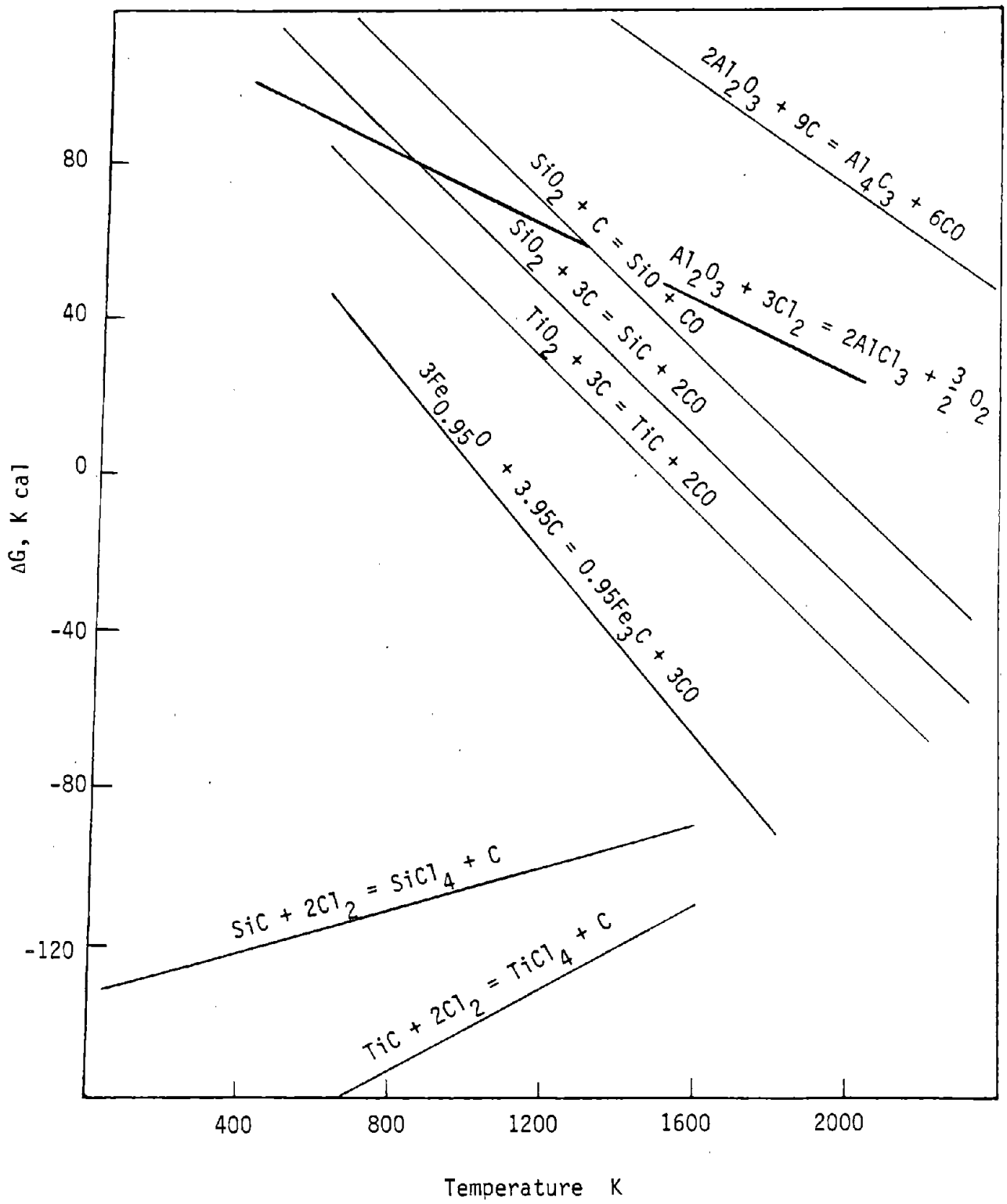

Figure 1. Gibbs energy values as a function of temperature

Table I. Analysis of Coal Wastes

	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	MgO	CaO	K_2O
Before treatment	52.5	17.8	2.7	0.7	1.0	1.4	2.2
After* Treatment	55.8	19.4	2.0	1.0	-	-	1.3

* Percentages correspond to a sample burned at 800°C and carbon content is 13.2%. L.O.I. at 800°C is 20.5%

2. Carbothermal reduction:

The overall reaction

$$(Al_2O_3, SiO_2) + 3C = Al_2O_3 + SiC + 2CO \qquad (2\text{-}1)$$

occurs rapidly at temperatures in the range 1500 to 1600°C. A study of the kinetics and mechanisms of reaction (2-1) showed that silicon monoxide is involved as an intermediate (3) . Thus, by mixing a limited amount of carbon with coal wastes in this reaction system only volatile silicon monoxide rather than solid silicon carbide was formed. Reaction (2-1) can be broken down further to show the formation of silicon monoxide and silicon carbide in the vicinity of the pellet (4):

$$(Al_2O_3, SiO_2) + C = Al_2O_3 + SiO + CO \qquad (2\text{-}2)$$

and

$$SiO + 2C = SiC + CO \qquad (2\text{-}3)$$

a) The effect of carbon content:

Based upon reaction (2-2) and silicon content in coal waste, the carbon originally contained in the pretreated sample is higher than the stoichiometric amount for this reaction (11.2%). However, since coal wastes contain α -quartz, various aluminosilicates, and other minor impurity minerals, the reactions occurring inside the pellet mixture are more

complicated than that represented by reaction (2-1). Free silica was reduced first, followed by the silica in the other aluminosilicates. Furthermore, the kinetics of reaction (2-3) is much faster than that of reaction (2-2). Therefore, it is difficult to calculate the exact stoichiometric amount of this reaction system.

Experimentally, if added carbon is more than about 7%, no silica remains in the product at the completion of reaction. As the carbon addition increases up to 25%, the amount of silicon carbide in the product increases. Also, Figure 2 shows that the largest alumina content in pellet product is 52% at 7% added carbon.

An important factor to consider is that the carbothermal reduction of silica in mullite requires much lower CO partial pressure and hence will be more difficult than the carbothermal reduction of other aluminosilicates. X-ray diffraction patterns indicate that carbothermal reduction under 7% added carbon mixture tends to produce mullite.

b) The effect of temperature:

The upper temperature limit of this reaction system is that temperature at which the reaction of alumina with carbon begins. And it is experimentally observed that mullite still remains below 1450^{o}C. For these reasons, the temperature range investigated was 1450-1550^{o}C.

Since this process is endothermic, raising the temperature increases reaction kinetics, as indicated by Figure 3. Consequently, the selective removal of silica by volatilization is most favorable at about 1550^{o}C.

c) The effect of pellet size:

Experiments have been performed with pellets varying in size between 4 to 12 mm in diameter. No significant difference was observed as shown in Figure 4. The reason for this is that heat penetration into the pellets and diffusion of SiO and CO gases out of the pellets are not greatly affected by pellet size in the range studied.

d) The result of X-ray analysis and microscopic examination:

The pellet diameter did not change during the reaction but the porosity increased substantially. Microscopic investigation confirmed the formation of

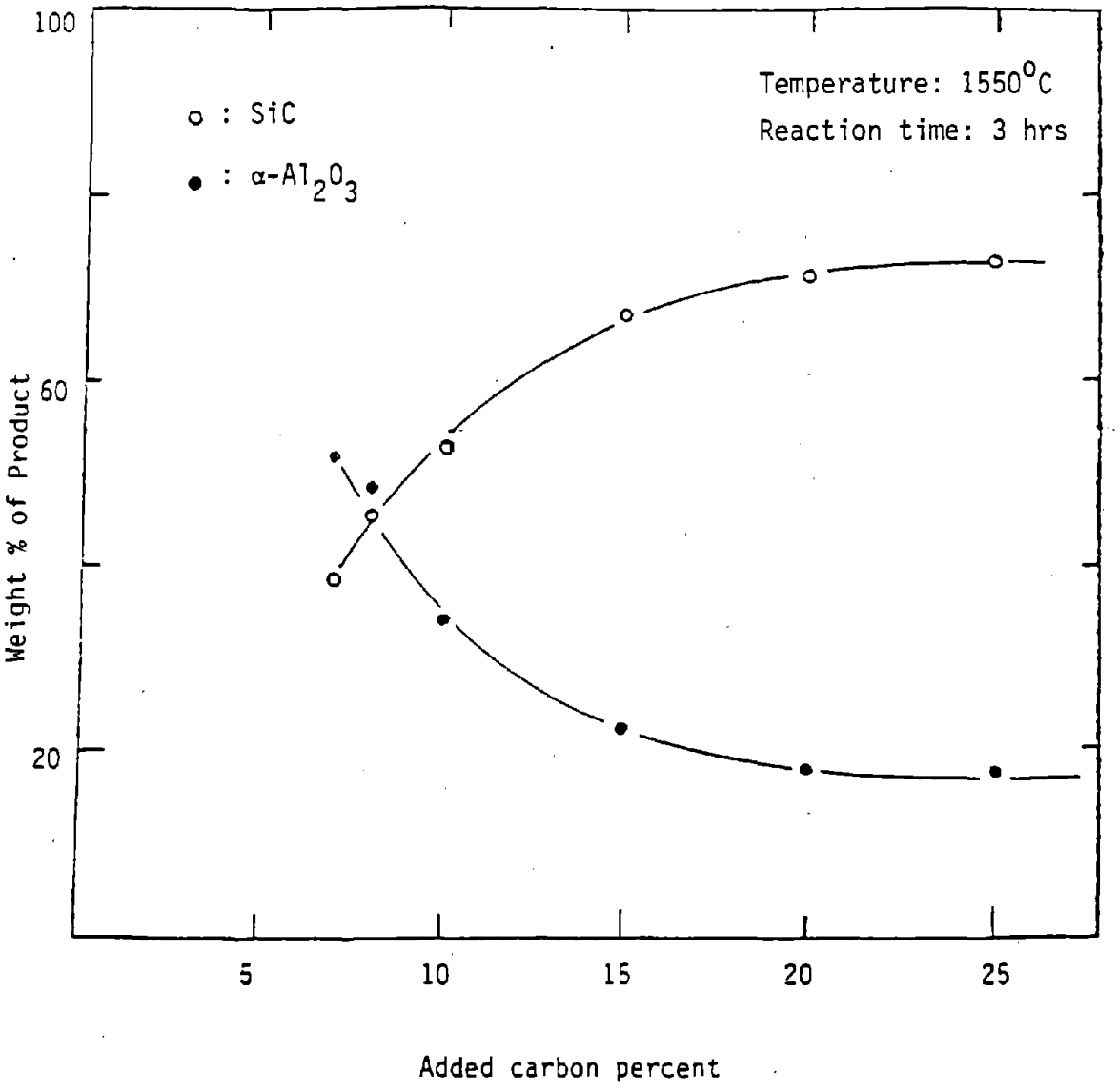

Figure 2. Effect of carbon content in carbothermal reduction

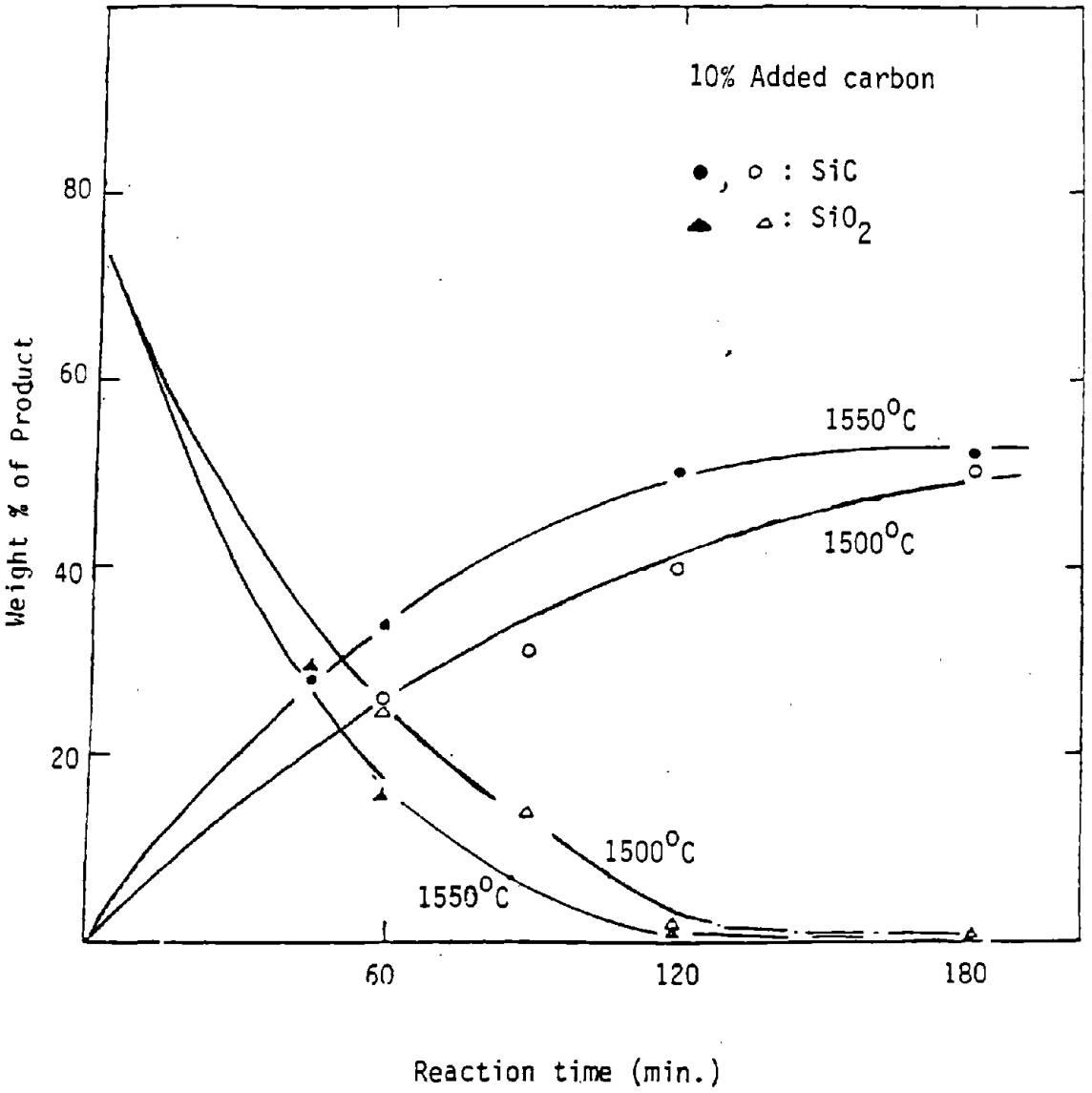

Figure 3. Effect of temperature and time in carbothermal reduction

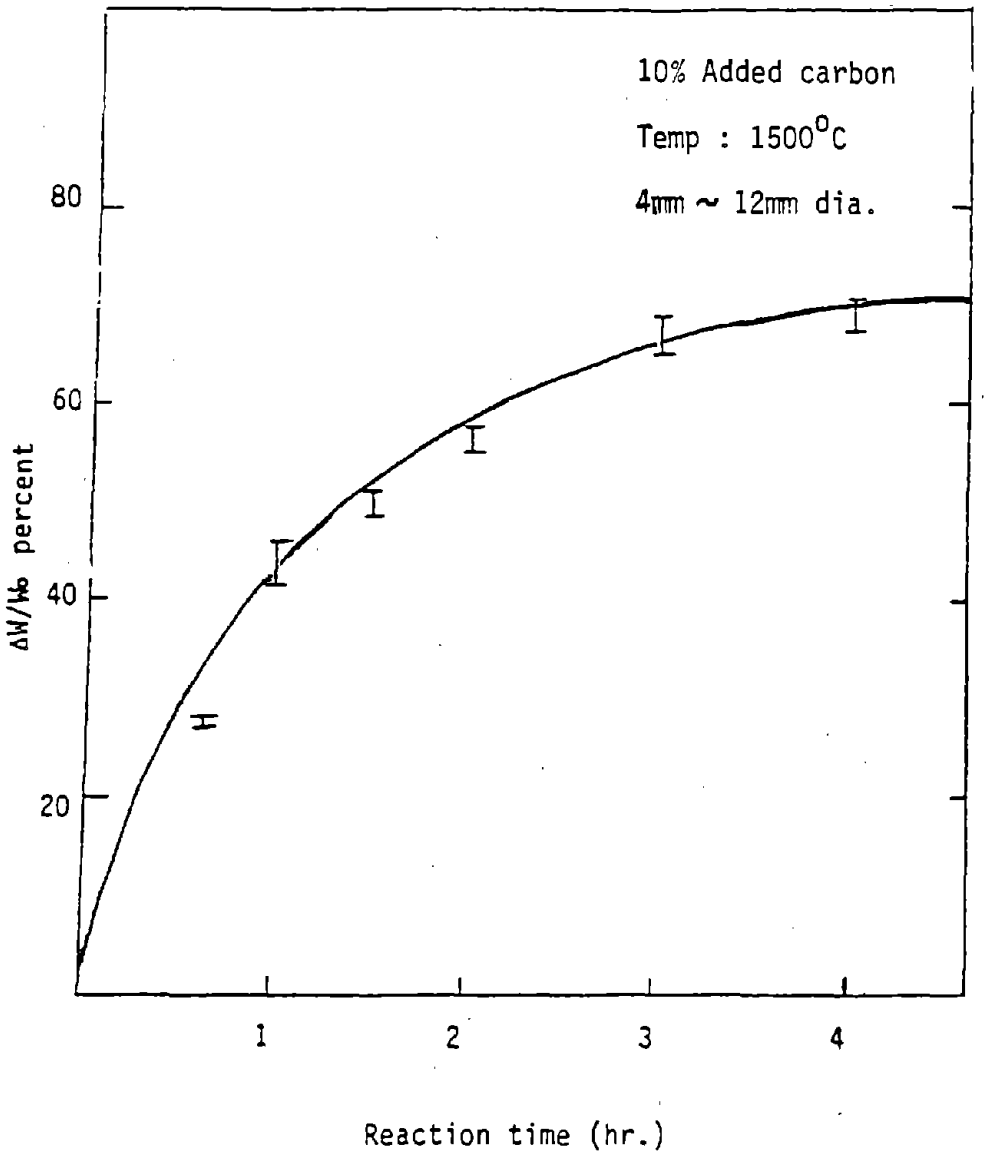

Figure 4. Weight change vs. time for pellets of various sizes

silicon carbide whiskers around the remaining alumina as seen in Figures 5 and 6.

X-ray diffraction studies for carbothermal reduction showed that the position of peak is constant but the intensity of peak changes with reaction conditions as seen in Figure 7.

3. Separation of alumina from the product mixture by the chlorination of silicon carbide:

Chlorination of silicon carbide to silicon tetrachloride is based on the following reaction (5) :

$$SiC + 2Cl_2 = SiCl_4 + C \qquad (3\text{-}1)$$

The Gibbs energy for the reaction of silicon carbide with chlorine gas is more negative than that for the chlorination of alumina. Consequently, the selective chlorination of silicon carbide from the product mixture can easily be performed without any loss of alumina in the temperature range 500 to 750^{o}C.

X-ray diffraction patterns of the product chlorinated at 650^{o}C revealed only alumina peaks, but EDAX and SEM photographs showed that a small amount of silicon carbide still remained in the product as shown in Figures 8 and 9, respectively.

In the preliminary study for selective chlorination, the alumina content was determined to be 92 to 96% by an atomic absorption analysis.

Parameters controlling this selective chlorination and optimum conditions need to be further determined.

FURTHER STUDY

1. Since the minor impurities contained in coal wastes affect the purification of the alumina product, their behavior (especially impurities containing Fe and Ti) needs to be investigated.

Figure 5: After carbothermal reduction (5% carbon content) x 2000
A: αAl_2O_3 and a small amount of mullite
S: SiC

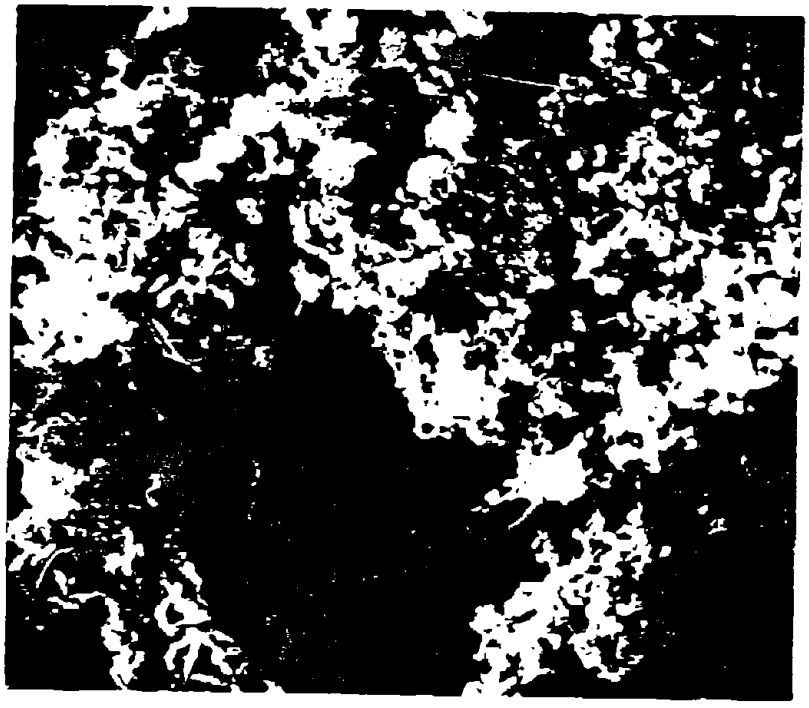

Figure 6: After carbothermal reduction (15% carbon content) x 2000
A: αAl_2O_3
S: SiC

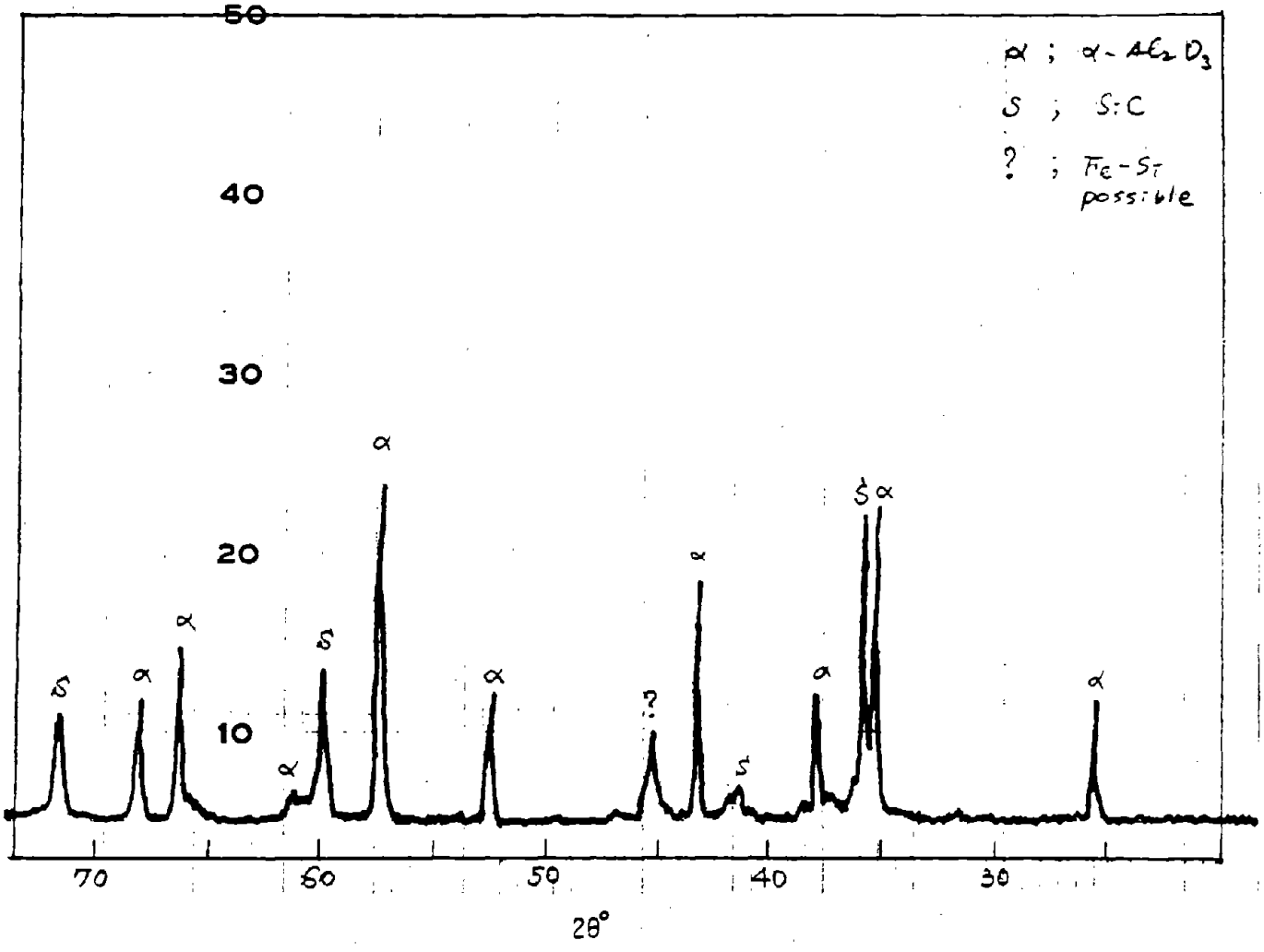

Figure 7. X-ray diffraction patterns (After carbothermal reduction)

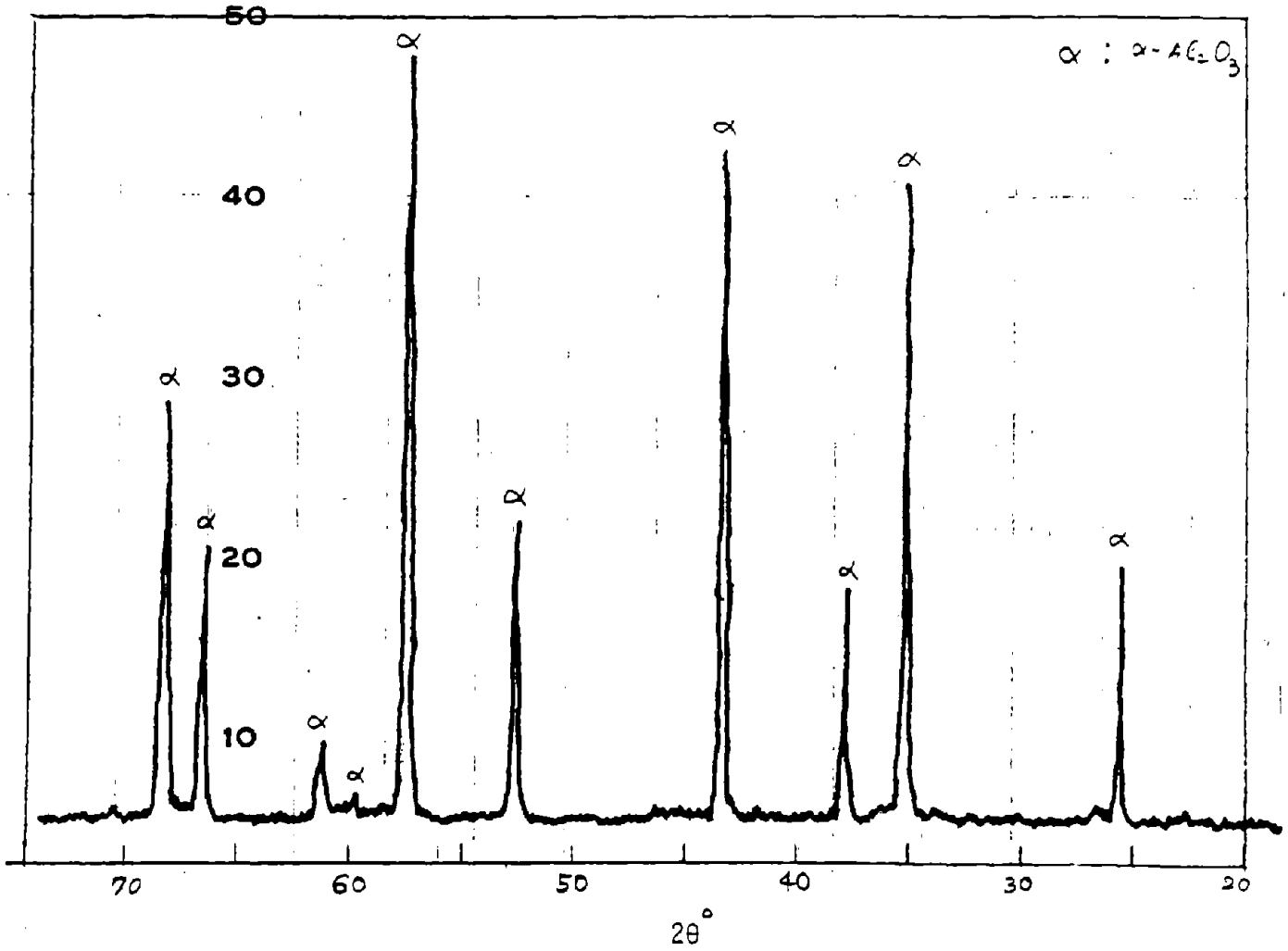

Figure 8. X-ray diffraction patterns (After chlorination)

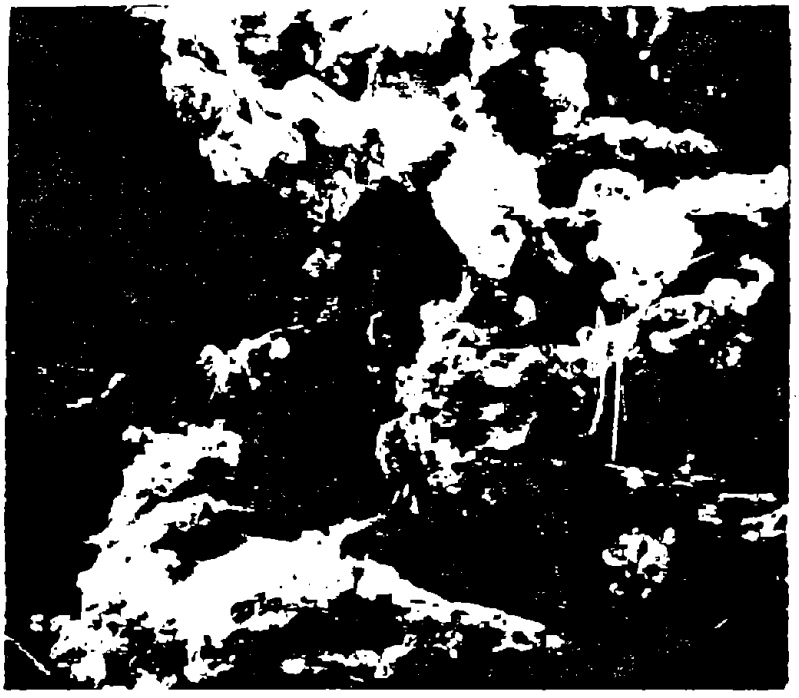

Figure 9. After chlorination of carbothermal product (x 2000)
A: αAl_2O_3
S: SiC

2. For the complete removal of silicon carbide by chlorination the kinetics and the optimum reaction conditions must be determined.

3. To lower the cost of separation of the silicon carbide and alumina, physical separation methods such as selective sedimentation and flotation must be studied.

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