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NEW DEVELOPMENTS IN THE LIME-SODA SINTER PROCESS FOR RECOVERY OF ALUMINA FROM FLY ASH*

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INTRODUCTION

Over 80 percent of the alumina produced in the United States is extracted from bauxite ore which is imported from developing countries. As a result of fiscal and political policy changes in these countries, bauxite reserves have become less secure as resources for consuming nations. The producing countries have nationalized mines, increased taxes and royalties, and instituted cartel-type price control. An International Bauxite Association (IBA) was formed in 1974 and its members account for 75 percent of the world's total bauxite production. Since the IBA was formed, the country of origin tax on bauxite to the United States from Jamaica, Haiti, and Surinam has increased from $2 to $20 per ton of bauxite ore. In addition, higher freight and labor charges have increased the cost of importing bauxite. 1,2/

The above factors have led to renewed interest in alumina production from raw materials other than bauxite. The United States would be well advised to encourage this development so as to assure future availability of aluminum. Today the Soviet Union has the only aluminum industry based partly on nonbauxite materials. The ore used is nepheline syenite, a waste product from the mining of apatite for phosphate fertilizer manufacture. The nepheline is mixed with limestone, then ground and sintered, producing dicalcium silicate and aluminates of sodium and potassium. The resulting sinter is pulverized and the alkali aluminates extracted using a solution of caustic soda. Aluminum hydroxide is precipitated from the extract by treatment with carbon dioxide, removed by filtration and then calcined to give alumina. Nepheline syenite deposits in Egypt have been investigated with Soviet assistance as possible sources of alumina for an aluminum plant in Egypt which is powered by electricity generated at the Aswan Dam. 1/

Tax and other bauxite cost increases have narrowed the gap in the United States to where the cost of producing alumina from nonbauxite materials could

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1. Patterson, Sam H., "Aluminum from Bauxite: Are There Alternatives?," American Scientist (1977).

2. Mitchell, Wilson D., "Bauxite and Alumina," Mining Engineering, March, 27 (1976).

become attractive. One of the promising nonbauxite raw materials of current interest is fly ash. Currently, about 50 million tons of fly ash, much of which contains significant amounts of alumina, are generated annually in the United States. 3/ Because the economics of nonbauxite processing are strongly influenced by energy considerations, a readily available raw material such as fly ash previously mined and crushed becomes particularly attractive.

Previous work has shown that alumina can be extracted from fly ash. 4,5,6/ The present investigation was undertaken to further this work by developing a more fundamental understanding of the lime-soda sinter reaction system. Two different coal fly ashes were used, one from a midwestern bituminous coal and the other from a western subbituminous coal. The results obtained are expected to be applicable to many of the fly ashes produced in the United States today.

The Alumina to be used in the manufacture of aluminum metal must be essentially iron-free. To help achieve this, the fly ashes used were magnetically separated and the nonmagnetic, low-iron fractions became the raw material for the lime-soda sinter tests. The magnetic separation was conducted using low intensity magnetic separation because only the highly susceptible magnetite and maghemite particles containing little alumina and silica were to be separated. The magnetic separator used is described in a previous paper. 7/ The compositions of the nonmagnetic fractions of the two fly ashes used are given in Table 1. Essentially no magnetic fraction was recovered from the subbituminous ash because of its low iron content.

The data in Table 1 show that the subbituminous coal fly ash has a high calcium content. If this calcium is reactive in the sinter reactions then less limestone will be required for processing, and the western coal fly ashes will have an economic advantage over other ashes.

THE LIME-SODA SINTER PROCESS

Sintering methods make use of lime for fixation of the silica and formation of soluble aluminate compounds. When soda ash is added to replace some of the

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3. Ash at Work, Vol. X, No. 4 (1978).

4. Chou, K. S., W. A. Klemm, M. J. Murtha, and G. Burnet, "The Lime-Sinter Process for Production of Alumina from Fly Ash," Proceedings, 4th International Ash Utilization Symposium, St. Louis, Energy Research and Development Administration MERC/SP-7614 (CONF-760322), 433 (1976).

5. Burnet, George, M. J. Murtha, and H. Wijatno, "Recovery of Alumina from Fly Ash by High-Temperature Chlorination," Proceeding, Third Kentucky Coal Refuse Disposal and Utilization Seminar, 83 (1977).

6. Kapoli, Laszlo, "Principles of Complex Utilization of Mineral Resources," Zesz. Nank. Akad. Gorn.-Hutn., Cracow, Ceram., 28, 7 (1975).

7. Murtha, M. J. and G. Burnet, "The Magnetic Fraction of Coal Fly Ash: Its Separation, Properties, and Utilization," Proceeding Iowa Acad. Sci., 85 (1), 10 (1978).

Table 1. Composition of Nonmagnetic Fractions of Bituminous and Subbituminous Coal Fly Ashes

	Chemical Composition, Wt. Percent Nonmagnetic Fraction of Coal Fly Ash	
Constituent	Bituminous (a)	Subbituminous (b)
SiO_2	47.99	30.18
Al_2O_3	20.61	19.71
Fe_2O_3	6.10	5.38
CaO	5.53	28.79
MgO	0.78	4.47
Na_2O	0.37	1.66
K_2O	1.88	0.32
TiO_2	0.83	1.51
SO_3	1.97	2.18
C	8.16	0.60
L.O.I.	10.80	0.71
Wt. % of Total Fly Ash	78.5	99.9

(a) Nonmagnetic fraction of fly ash from Lakeside Power Plant, Milwaukee, Wisconsin. Fly ash of coal from western Kentucky and southern Illinois was collected by mechanical precipitators.

(b) Whole fly ash from Comanche Power Plant, Pueblo, Colorado. Fly ash of coal from Gillette, Wyoming, was collected by electrostatic precipitators.

lime, sodium aluminate is also formed. The aluminates are dissolved from the pulverized sinter in an aqueous soda ash solution, and then precipitated as aluminum trihydrate which is separated and calcined to alumina.

During the sinter reaction it appears that limestone reacts with the silica to form dicalcium silicate and carbon dioxide:

$$2\ CaCO_3 + SiO_2 \rightleftarrows 2CaO \cdot SiO_2 + 2\ CO_2 \qquad (1)$$

The formation of dicalcium silicate frees the alumina that was combined with the silica. This alumina then reacts with either soda ash or limestone to form sodium aluminate or calcium aluminates respectively. The desired calcium aluminate is $C_{12}A_7$, the most soluble of the calcium aluminate compounds. The following reactions show the desired reactions to obtain high yields of soluble aluminates from the sinter:

$$12\ CaCO_3 + 7\ Al_2O_3 \rightleftarrows 12CaO \cdot 7Al_2O_3 + 12\ CO_2 \qquad (2)$$

$$Na_2CO_3 + Al_2O_3 \rightleftarrows Na_2O \cdot Al_2O_3 + CO_2 \qquad (3)$$

The quantity of limestone which reacts with the alumina is important. If either more or less than the optimum amount of limestone reacts, the recovery of alumina will be reduced. As the amount of limestone in the sinter mixture is increased the following progression of calcium aluminate compounds results: Gehlenite ($2CaO \cdot Al_2O_3 \cdot SiO_2$), $CaO \cdot Al_2O_3$, $12CaO \cdot 7Al_2O_3$, and $3CaO \cdot Al_2O_3$. Gehlenite is insoluble and neither CA or C_3A are as soluble as $C_{12}A_7$. The reduced recovery of alumina from CA and C_3A is due to the formation and precipitation of insoluble calcium aluminum hydrates during the extraction step. 8/ The limestone in the sinter material can combine with both the silica and the alumina in the fly ash, and an exacting ratio of limestone, silica, and alumina is required for maximum alumina solubilization.

When soda ash is also in the sinter, sodium silicate and sodium aluminate can form. The soda ash can combine with the alumina, increasing the yield of soluble aluminate. If sodium silicate forms it is also soluble and the dissolved silica will precipitate from the extract as aluminum silicates, removing dissolved alumina from solution. Thus, the ratios of fly ash, limestone, and soda ash in this sinter also greatly influence overall recovery of soluble aluminates.

EXPERIMENTAL PROCEDURE AND RESULTS

The experimental method used for sintering consisted of first forming pellets from the sinter ingredients which had been blended in a ball mill. The pellets were 0.5 inch in diameter and each contained 2.5 grams of sample. Sintering was carried out in a heavy-duty electric tube furnace. Several pellets in a platinum boat were inserted gradually into the furnace tube and brought to 800 C. The samples were then heated at a constant rate of 3.6 C/min. and subjected to a one

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8. Lundquist, R. V. and H. Leitch, "Two Hydrated Calcium Aluminates Encountered in the Lime-Soda Sinter Process," U.S. Bureau of Mines Rep. of Invest. No. 6335 (1963).

hour soak time at the desired sintering temperature. The soluble aluminates were extracted from the pulverized sinter and the extract was analyzed for aluminum content by a complexometric titration.

A dilute soda ash solution was used to dissolve the calcium and sodium aluminates from the sinter. The calcium reacts with carbonate ions to form a calcium carbonate precipate. Precipitation of calcium carbonate is required for complete dissolution of the calcium aluminates. A dilute solution of sodium carbonate provides nearly the optimum pH for keeping alumina in solution while minimizing the dissolution of silica.

BITUMINOUS COAL FLY ASH SINTERS

The nonmagnetic fraction of the fly ash from a bituminous coal was used in the preparation of nineteen lime-soda fly ash sinters. The percentages of extractable alumina over a range of sintering temperatures were determined for each composition. These data are given in Table 2 and in Figures 1, 2, and 3.

The influence of sinter composition on the percentage of soluble alumina formed is evident in Figures 1, 2, and 3. The data are shown as curves of constant alumina recovery as a function of sinter composition for three sintering temperatures. It is clear that the quantities of limestone and soda ash must be carefully controlled to assure optimum alumina recovery. Either an excess or deficiency of limestone or soda ash will reduce the yield of alumina.

Figure 4 relates sinter composition to maximum recovery and permits calculation of the compound ratios formed. Values read from the points of maximum solubilization for each lime to silica mole ratio sinter composition on Figures 2 and 3 provide the data for Figure 4. The effect of sinter temperature in the range 1100 to 1300 C is not large; the maximum yield values at 1200 C and 1300 C are nearly equal and somewhat higher than at 1100^{o} C.

The equation for the linear relationship between the $Na_2O \cdot Al_2O_3$ mole ratio and the $CaO \cdot SiO_2$ mole ratio for the data of Figure 4 is:

$$Na_2O \cdot Al_2O_3 = 6.42 - 2.40\ CaO \cdot SiO_2 \qquad (4)$$

When the molar concentrations of alumina and silica in the bituminous coal fly ash are substituted into equation 4, the results indicate (1) that calcium aluminate $C_{12}A_7$ is replaced in the product by $Na_2O \cdot Al_2O_3$ as soda ash is substituted for limestone in the sinter mixture, and (2) that about 2.3 moles of lime combine with each mole of silica. The maximum yields thus consist of calcium silicates in a mole ratio of 2.3 $CaO:SiO_2$ plus varying quantities of $Na_2O \cdot Al_2O_3$ and of calcium aluminates in the mole ratio $C_{12}A_7$. Equivalent lime-soda-fly ash sinter reactions for equation 4 are

$$SiO_2 + 2.3\ CaCO_3 == 2.3CaO:SiO_2 + 2.3\ CO_2 \qquad (5)$$

$$7\ Al_2O_3 + 12\ CaCO_3 == 12CaO \cdot 7Al_2O_3 + 12\ CO_2 \qquad (6)$$

$$Al_2O_3 + Na_2CO_3 == Na_2O \cdot Al_2O_3 + CO_2 \qquad (7)$$

The molar ratio of silica to alumina in the nonmagnetic fraction of the bituminous coal fly ash is 4.2. If this ratio is higher, more than 2.3 moles if CaO per mole of SiO_2 will be needed for optimum alumina recovery.

Table 2. Alumina Extraction from Lime-Soda Sinters of Bituminous Coal Fly Ash.

Molar Composition	Alumina Recovery, Percent		
$\frac{CaO}{SiO_2}$ and $\frac{Na_2O}{Al_2O_3}$	Sintering Temperature		
	1100°C	1200°C	1300°C
1.8 - 1.2	10.09	4.22	1.53
2.0 - 0.6	32.59	19.29	15.97
2.0 - 0.8	57.72	56.73	48.03
2.0 - 1.0	49.90	81.94	68.24
2.0 - 1.2	80.80	91.17	84.51
2.2 - 0	33.01	21.37	4.53
2.2 - 0.4	33.80	30.06	26.34
2.2 - 0.8	77.50	79.63	67.01
2.2 - 1.2	98.32	91.76	99.81
2.4 - 0	27.62	39.83	36.36
2.4 - 0.3	42.73	61.99	55.74
2.4 - 0.7	75.47	89.54	82.83
2.5 - 0	23.52	44.63	48.80
2.5 - 1.0	82.37	76.67	78.33
2.6 - 0.2	27.10	83.46	79.59
2.6 - 0.6	63.75	66.73	57.98
2.6 - 1.0	50.54	61.28	66.34
2.7 - 0	24.43	35.77	41.76
2.7 - 0.1	58.77	64.53	69.00

SUBBITUMINOUS FLY ASH SINTERS

Fly ash from subbituminous coal normally has a lower mole ratio of silica to alumina than that found in fly ash from bituminous coal. The calcium content, on the other hand, is usually much higher. Because these conditions exist, less limestone is required when subbituminous coal fly ashes are used. This will improve the economics of alumina recovery.

The iron content of the subbituminous coal fly ash used in this investigation was so low that essentially no magnetic fraction was obtained when the ash was run through the magnetic separator. The sinter mixtures were thus prepared using the total ash. The experimental procedure used was the same as that for the bituminous coal ash. Twenty different sinter compositions were prepared to again determine curves of constant alumina extraction as a function of lime-soda-fly ash ratios. The yields of alumina over a range of sintering temperatures were found for each composition. The data for 47 runs are given in Table 3 and Figures 5 and 6.

The relationships between sinter composition and alumina yield at two different temperatures are shown in Figures 5 and 6. As was the case with the bituminous coal fly ash sinters, either an excess or deficiency of limestone and/or soda ash reduces the recovery of alumina. It is important to note that there is no apparent difference in reactivity between the calcium contained in the fly ash and that in the added limestone. As was the case for the bituminous fly ash sinters, a linear relationship results when the maximum recovery of alumina is plotted as a function of sinter composition. For the subbituminous ash sinter, the equation is as follows:

$$Na_2O{\cdot}Al_2O_3 = 5.12 - 1.69\ CaO{:}SiO_2 \qquad (8)$$

An examination of equations 4 and 8 fails to disclose any similarity for the two types of fly ash. Significant differences should be expected because the subbituminous ash has a much lower silica to alumina mole ratio: 2.6 compared to 4.2 for the bituminous ash. When the concentrations of alumina and silica in the subbituminous coal fly ash are substituted into equation 8, it is found that the product consists of compound mixtures in the following molar ratios:

$$2.4CaO{:}SiO_2,\ 1.1Na_2O{:}Al_2O_3,\ \text{and}\ 12CaO{\cdot}7Al_2O_3$$

This is in very close agreement with the compounds calculated as being present in the bituminous coal fly ash sinters.

Several additional coal fly ashes from bituminous, subbituminous, and lignite coals have been examined. Sinter mixtures were prepared for each of these fly ashes using formulations calculated from equations 4 or 8, as appropriate. After sintering, alumina recoveries greater than 90 percent were obtained in every case, as would have been predicted. Data for these tests are given in Table 4.

DISCUSSION OF RESULTS

The work reported in this paper shows that high percentages of alumina can probably be recovered from any bituminous or subbituminous coal fly ash if the proper sinter compositions and sintering temperatures are used. The sinter

Table 3. Alumina Extraction from Lime-Soda Sinters of Subbituminous Coal Fly Ash.

Molar Composition $\frac{CaO}{SiO_2}$ and $\frac{Na_2O}{Al_2O_3}$	Alumina Recovery, Percent (Sintering Temperature) 1100°C	1200°C	1300°C
1.8 - 1.6	84.78	82.79	
1.8 - 1.8	88.73	88.10	
1.8 - 2.0	89.60		
2.0 - 1.2	87.81	88.12	77.82
2.0 - 1.4	88.80	88.55	
2.0 - 1.6	88.50	88.51	73.05
2.0 - 1.8	92.77	93.95	
2.0 - 2.0	86.77		
2.2 - 0.8	65.95	58.70	70.77
2.2 - 1.2	92.89	88.44	
2.2 - 1.4	90.77	91.33	72.41
2.2 - 1.6	94.88	93.45	
2.2 - 1.8	73.62		
2.4 - 0.8	84.23	86.11	73.00
2.4 - 1.0	91.75	90.14	61.56
2.4 - 1.2	91.87	91.02	78.37
2.4 - 1.4	75.59	80.30	
2.4 - 1.6	58.94	75.50	86.90
2.6 - 0.8	91.55	88.35	80.49
2.6 - 1.2	84.67	71.54	70.04

Table 4. Recovery of Alumina Using Lime-Soda Sinters for Other Coal Fly Ashes.

Fly Ash Type	Sinter Molar Composition	Alumina Recovery, Percent		
(Wt % Al_2O_3, CaO, SiO_2)	$\frac{CaO}{SiO_2}$ and $\frac{Na_2O}{Al_2O_3}$	Sintering Temperature		
		1100^oC	1200^oC	1300^oC
Bituminous (a)	2.2 - 1.2	83.58	79.73	85.64
(28.3, 1.57, 52.1)	2.0 - 1.4	88.03	91.33	91.93
	2.5 - 1.0	67.76	61.06	
	2.4 - 1.1	64.82	60.34	64.72
Subbituminous (b)	2.2 - 1.2	91.46	82.35	85.66
(31.76, 1.92, 55.67)	2.0 - 1.4	87.83	94.73	76.03
	2.5 - 1.0	85.47	79.72	
	2.4 - 1.1	84.30	75.04	73.90
Lignite (c)	2.2 - 1.2	89.49	93.35	91.61
(19.10, 10.00, 59.61)	2.5 - 1.0	79.37	71.90	

(a) Nonmagnetic fraction of fly ash from TVA Kingston Steam Plant.

(b) Whole fly ash from Mexican coal mined across border from Eagle Pass, Texas.

(c) Whole fly ash from Monticello Power Station, Mt. Pleasant, Texas.

mixture must contain 2.3 to 2.4 moles of lime per mole of silica and a combination of 12 moles of lime per 7 moles of alumina for part of the alumina and 1 to 1.1 moles of soda per mole of alumina for the remainder. Under these conditions, 90 percent or more of the alumina can be extracted.

The maximum alumina recovery from bituminous coal fly ash took place at 1300 C while that for subbituminous coal ash occurred at 1100 C. When subbituminous coal fly ash sinters were heated to 1300 C, complete melting took place. There is evidence from other tests that satisfactory yields from some subbituminous coal fly ashes can be obtained at temperatures as low as 900 C.

The economics of the lime-soda sinter process will be effected by the type of fly ash used. In addition to the percentage of alumina in the ash, the concentration of contained calcium and the required sintering temperature are important factors. The utilization of higher calcium content fly ash will reduce the quantity of limestone required and will also decrease the amount of sinter residue to be disposed of.

A feasibility cost estimate made for the process has given costs of $150 to $180 per ton of alumina, with the lower cost for a high-calcium subbituminous coal fly ash. The estimates assumed that the fly ash was purchased at $5 per ton, and that no credit was taken for either the magnetic fraction of the fly ash or the sinter residue material. In reality, the fly ash is of negative value to the utility company, the magnetic fly ash fraction may be marketable as dense media for coal or ore washing, and the sinter residue has several potential uses. 9,10/ A utility company processing fly ash as a means of disposal, and selling a portion of the by-product materials, could produce alumina for a cost low enough to show a profit in view of the present selling price of $193 per ton. 11/

In summary, alumina can very likely be recovered from any coal fly ash by using the lime-soda sinter process and the proper proportions of raw materials. Process economics will be determined by the percentage of alumina in the fly ash, by the availability of limestone, by energy costs and by the ability to market the process by-products. The bituminous fly ashes generally contain a magnetic fraction which is not only a usable material as dense media for coal and ore washing, but has been found to be superior to magnetite, the material normally used. 12/ This material would be marketable today at $70 to $100 per ton. The

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9. Grzymek, Jerzy, "Prof. Grzymek's Self-Disintegration Method for the Complex Manufacture of Aluminum Oxide and Portland Cement," Light Metals, 2, 29 (1976).

10. Archibald, F. R. and C. M. Nicholson, "Alumina from Clay by the Lime-Sinter Method II," Metals Technology, June, 14 (1948).

11. Chemical Marketing Reporter, Oct. 2 (1978).

12. Roy, N. K., M. J. Murtha, and G. Burnet, "Use of the Magnetic Fraction of Fly Ash as a Heavy Medium Material in Coal Washing," Proceedings, 5th International Ash Utilization Symposium, Atlanta (1979).

sinter residue after extraction consists of calcium silicates and is chemically very similar to Portland cement. The residue can be converted to Portland cement by sintering with additional limestone and gypsum. A reduced amount of energy is required for this because much of the calcium and silica have already been converted to silicate form. Other uses of the sinter residue include agricultural liming, structural subbase material, processing into artificial aggregate, and application in ceramics and glass production. 9,10/

ACKNOWLEDGEMENT

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Figure Captions

Figure 1. Alumina Solubility as a Function of Lime-Soda Sinter Composition for Bituminous Coal Fly Ash; Sintered One Hour at 1100°C.

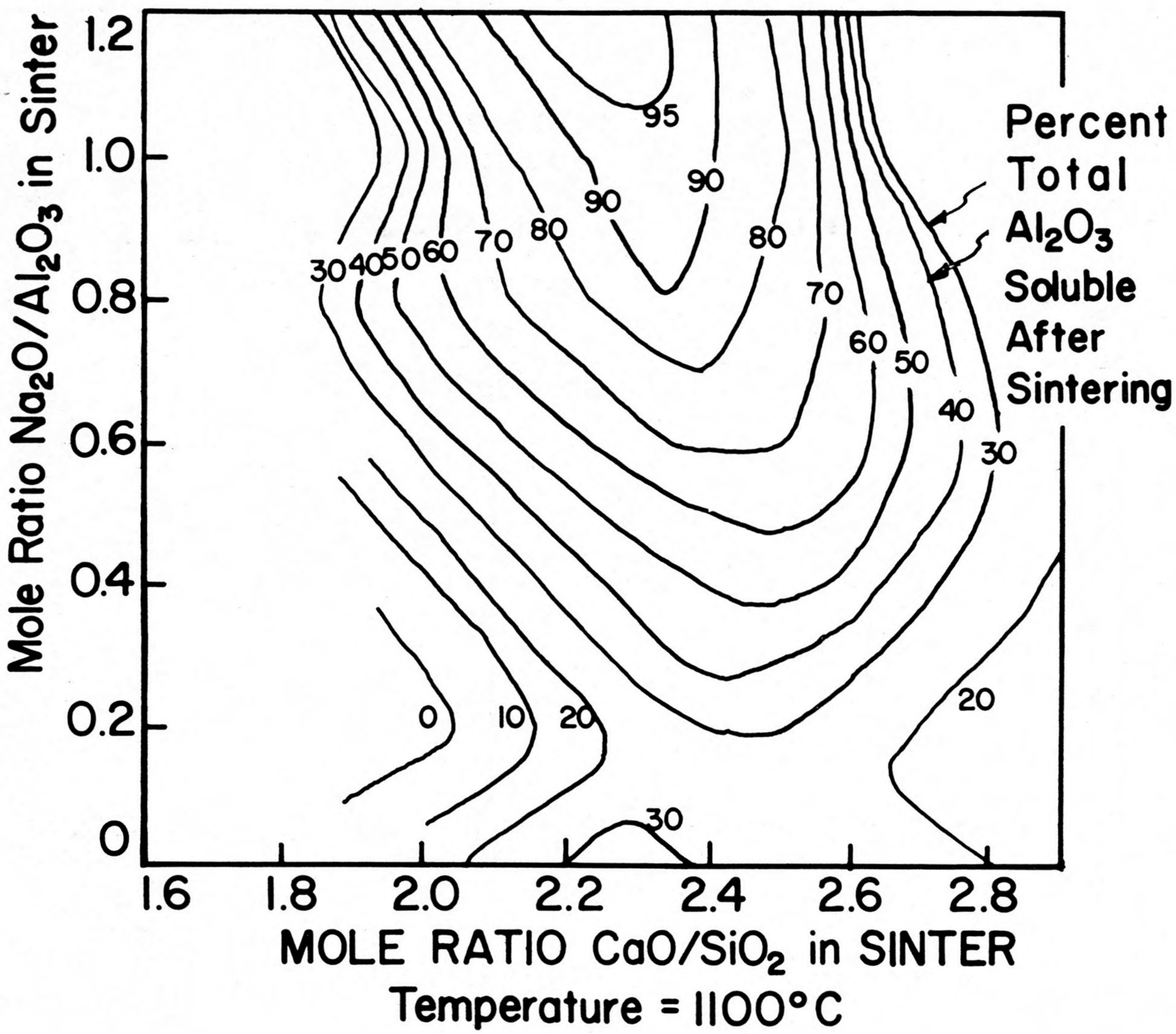
Figure 2. Alumina Solubility as a Function of Lime-Soda Sinter Composition for Bituminous Coal Fly Ash; Sintered One Hour at 1200°C.

Figure 3. Alumina Solubility as a Function of Lime-Soda Sinter Composition for Bituminous Coal Fly Ash; Sintered One Hour at 1300°C.

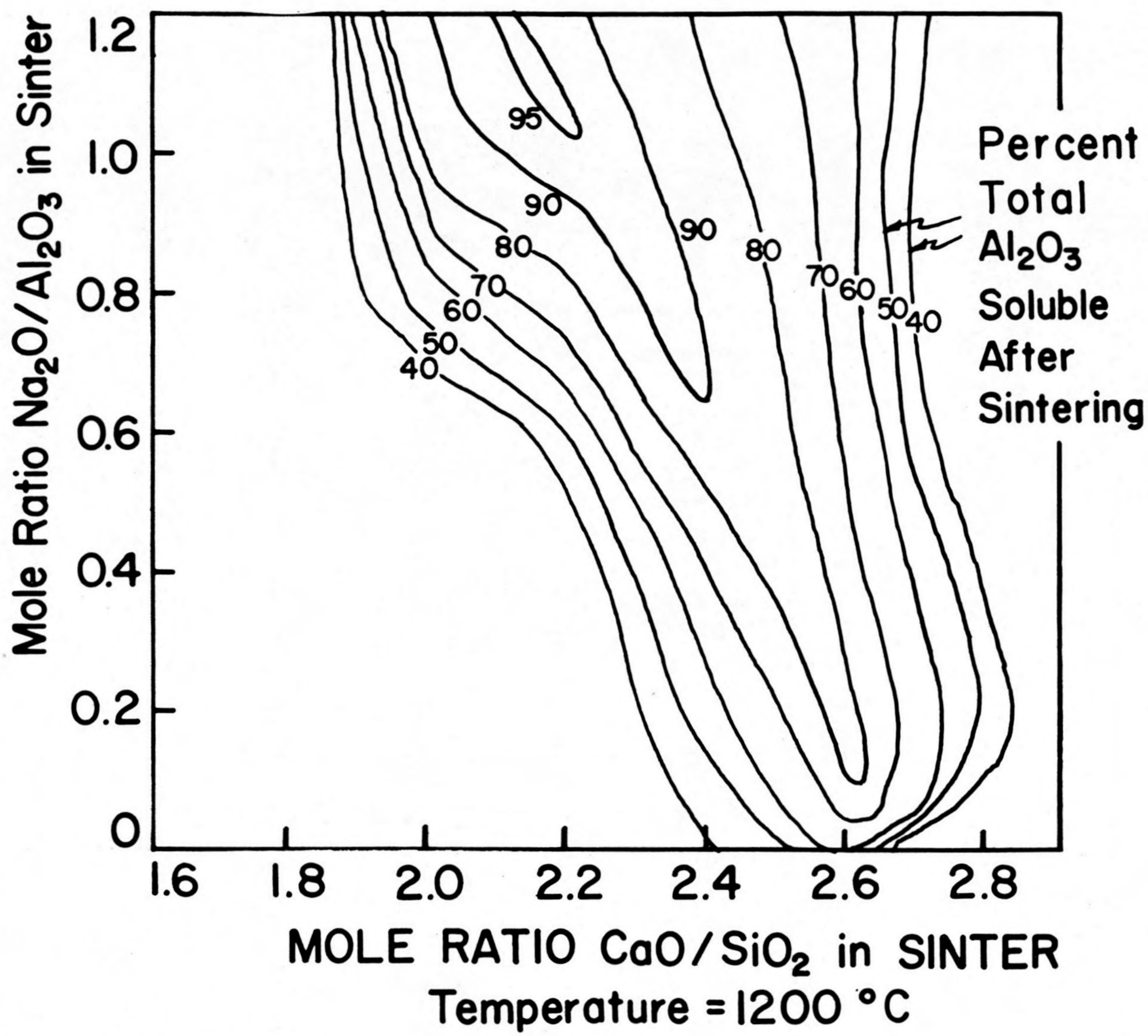
Figure 4. Sinter Compositions which Yield Maximum Alumina Recoveries for One Hour Sintering Time; Composite for Runs at 1200°C and 1300°C.

Figure 5. Alumina Solubility as a Function of Lime-Soda Sinter Composition for Subbituminous Coal Fly Ash; Sintered One Hour at 1100°C.

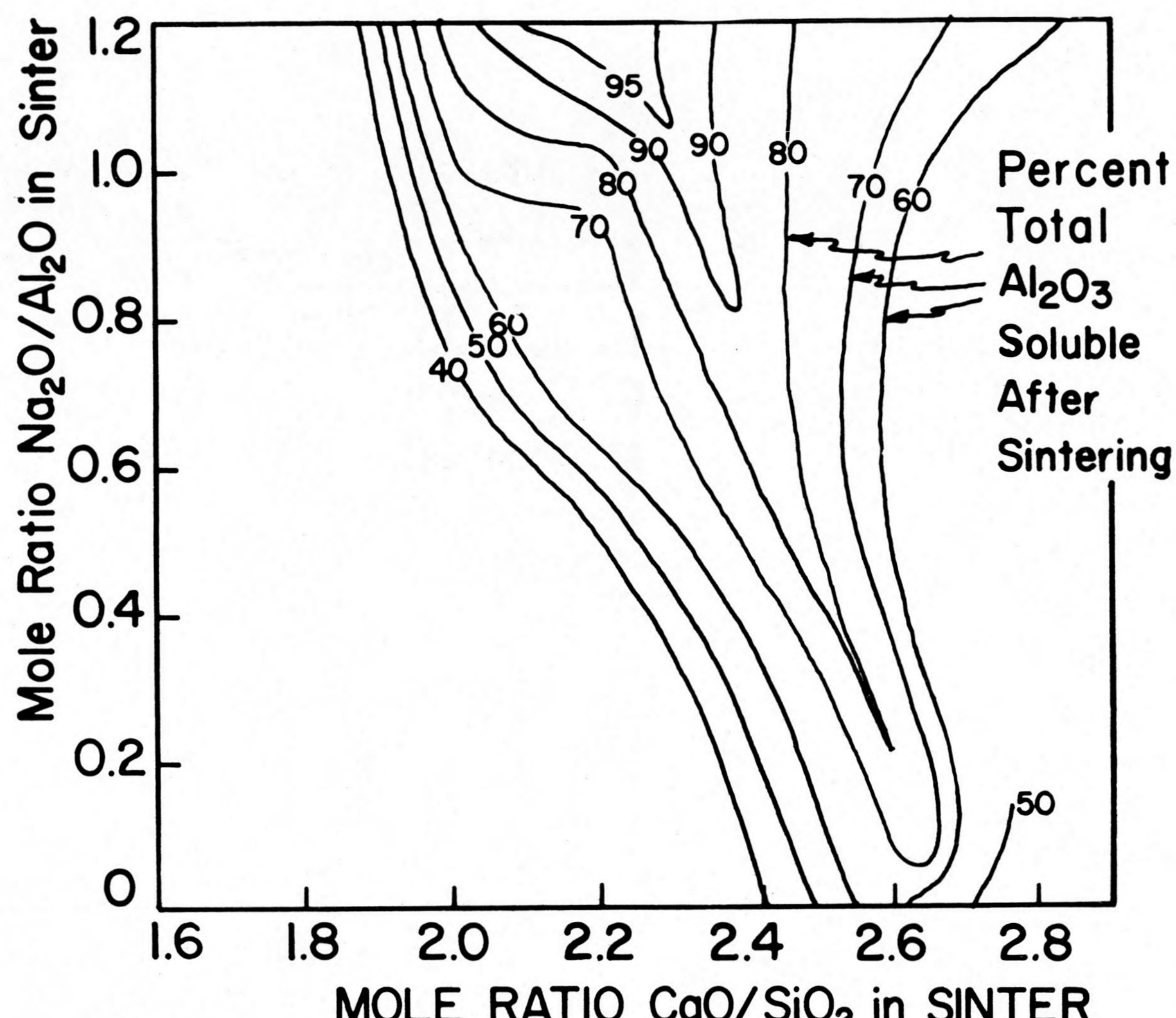
Figure 6. Alumina Solubility as a Function of Lime-Soda Sinter Composition for Subbituminous Coal Fly Ash; Sintered One Hour at 1200°C.



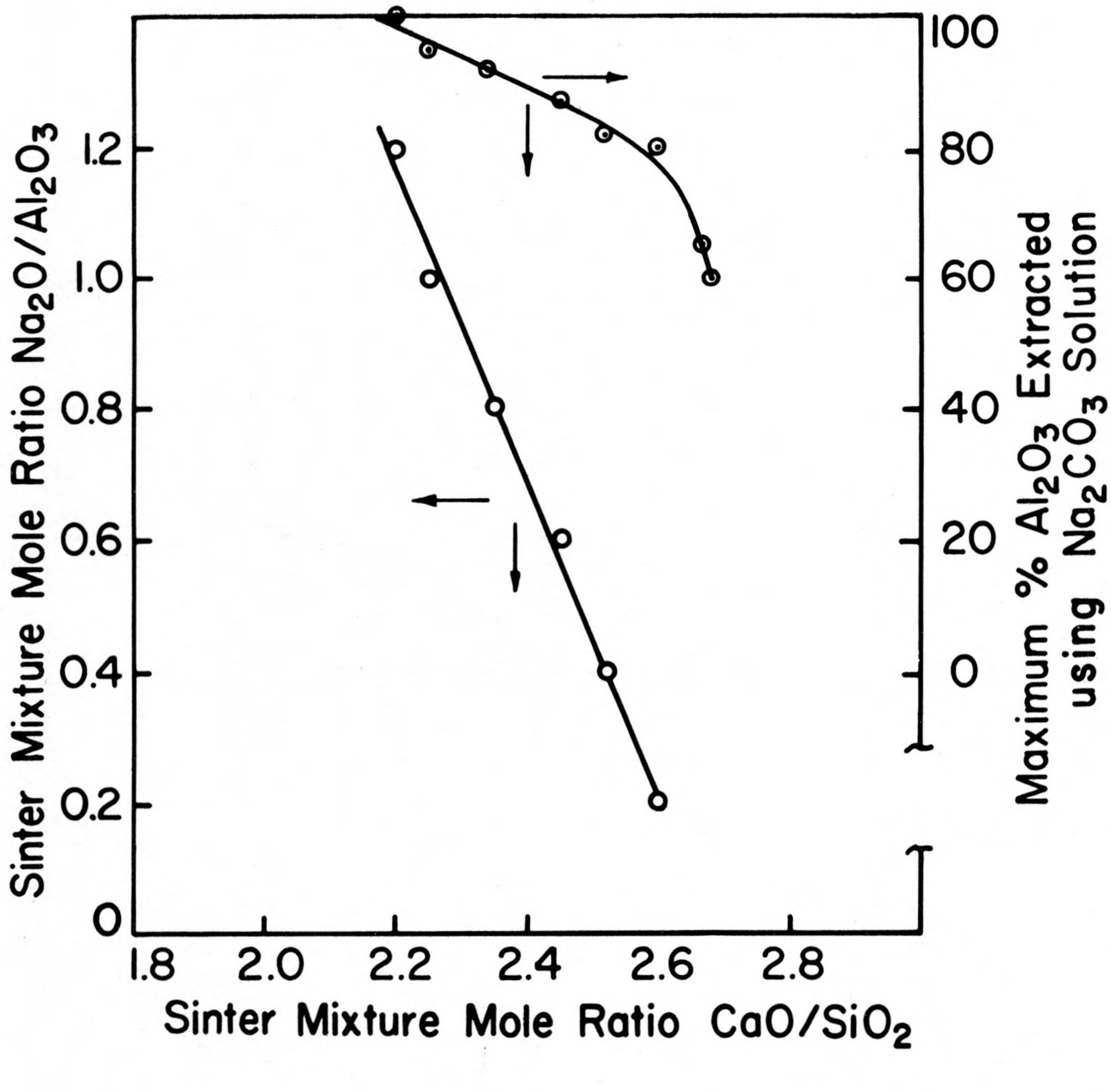
Mole Ratio Na_2O/Al_2O_3 in Sinter
1.2
1.0
0.8
0.6
0.4
0.2
0
1.6
1.8
2.0
2.2
2.4
2.6
2.8
MOLE RATIO CaO/SiO_2 in SINTER
Temperature = 1100°C
Percent Total Al_2O_3 Soluble After Sintering
95
90
90
90
80
80
70
70
60
60
50
50
40
40
30
30
30
20
20
10
0



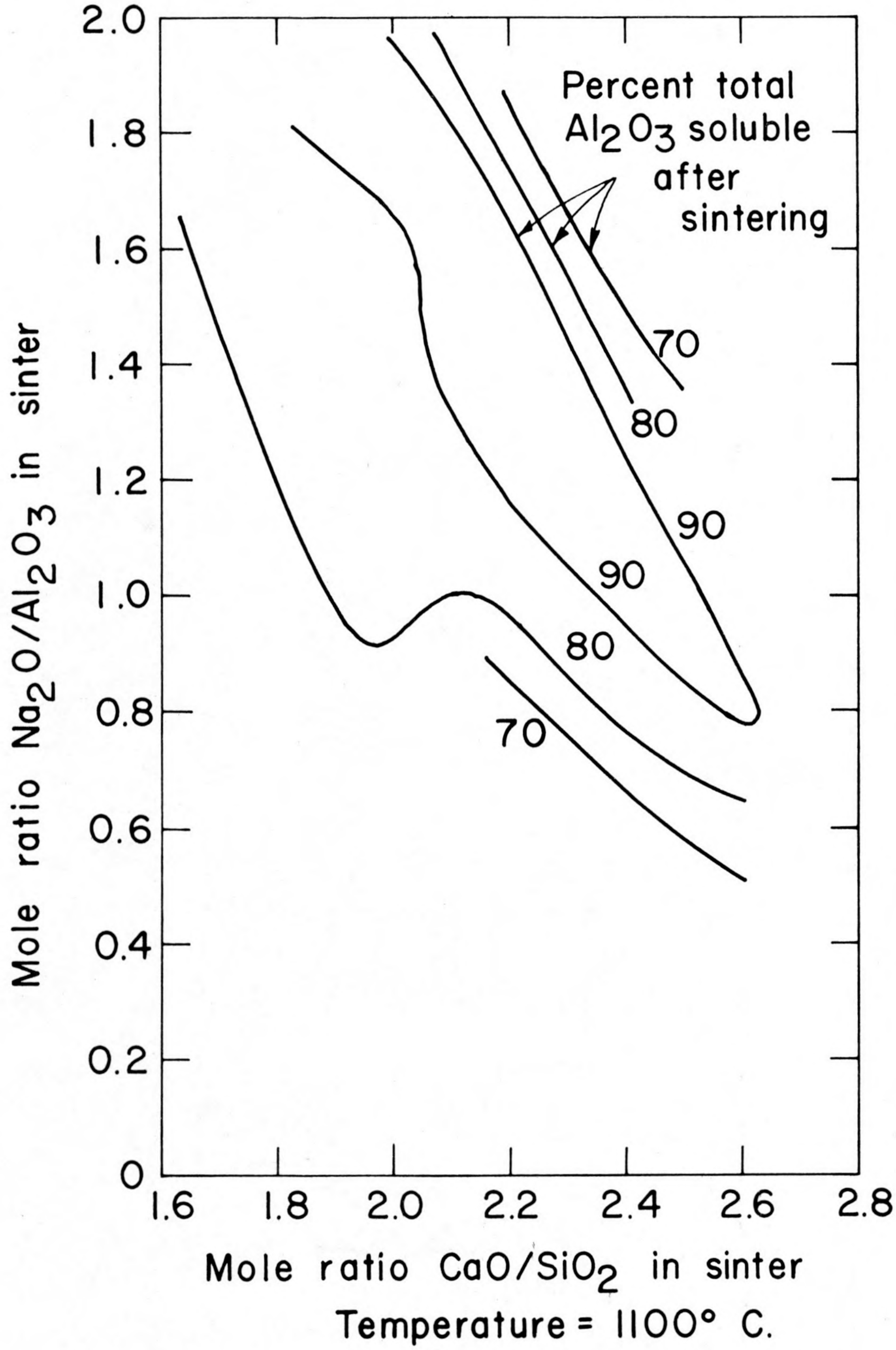
Mole Ratio Na2O/Al2O3 in Sinter
1.2
1.0
0.8
0.6
0.4
0.2
0
95
90
80
70
60
50
40
Percent
Total
Al2O3
Soluble
After
Sintering
1.6
1.8
2.0
2.2
2.4
2.6
2.8
MOLE RATIO CaO/SiO2 in SINTER
Temperature = 1200 °C



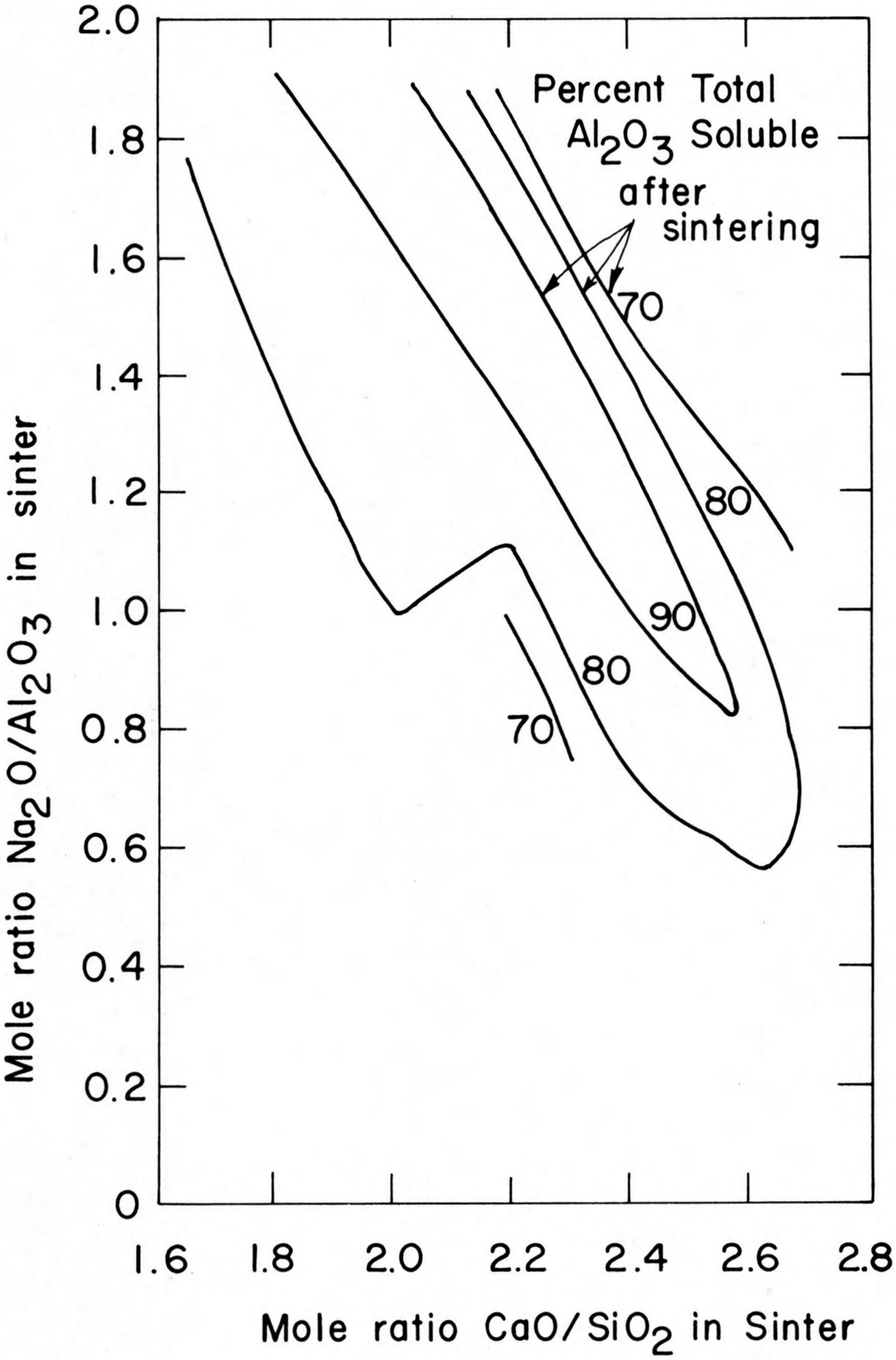
Temperature = 1300°C



Sinter Mixture Mole Ratio Na_2O/Al_2O_3
0
0.2
0.4
0.6
0.8
1.0
1.2
1.8
2.0
2.2
2.4
2.6
2.8
Sinter Mixture Mole Ratio CaO/SiO_2
100
80
60
40
20
0
Maximum % Al_2O_3 Extracted
using Na_2CO_3 Solution



Temperature = 1100° C.



Temperature = 1200° C.