Report to

DEPARTMENT OF ENERGY
Washington, D.C.

Use of Precalciners
to Remove Alkali from Raw Material
in the Cement Industry
Quarterly Technical Progress Report
May - June 1979

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Submitted by

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August 1979

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Quarterly Technical Progress Report
May-July 1979
Use of Precalciners to Remove Alkalies from
Raw Materials in the Cement Industry

DOE Contract No. EM-78-C-02-4929
PCA Contract No. CR-7574-4330

by
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1. Summary

This report covers part of a series of laboratory tests on high-alkali clays, feldspars, and similar argillaceous minerals, designed to determine the optimal method for volatilizing the alkalies contained in these compounds.

The major conclusions of this report are as follows:

1. Magnesium chloride is much more effective in removing alkalies from feldspars (especially at 1100°C) than from the other minerals. The soda-feldspar, albite, responded better than the potash-feldspar.
2. In the presence of CaCO_3 and CaCl_2 , reducing conditions appear to increase alkali volatility in the case of the feldspars. However, illite and muscovite behave peculiarly, losing more alkali when treated with solid graphite than when treated in a methane atmosphere.
3. Increasing the fineness of the minerals appeared to have a small negative effect on alkali volatility. This may have been due to surface sintering.
4. High temperatures (1450°C) caused melting of the mineral/ CaCl_2 / CaCO_3 mixtures. Initial alkali loss was

high, but very little further loss occurred once the melt had formed.

5. Water vapor had a negative effect on alkali volatility (from mixtures with CaCO_3 and CaCl_2). This may have been due to loss of HCl from the sample.
6. $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ as an admixture is not very effective in promoting alkali volatilization.

The fact that rapid alkali removal can be achieved by heating to 1450°C is encouraging. This suggests that alkali removal might be achievable using some kind of "flash-calcination" method. Clearly, the shorter the treatment period, the smaller the reaction vessel required.

2. Alkali Volatilization Studies (Task III)

Experiments have continued, using small (2-3 gram) samples of pure minerals plus chloride-containing admixtures heated in a controlled atmosphere in the 2" diameter tube furnace. Various atmospheres have been used.

2.1 Burns with an $\text{MgCl}_2/\text{NH}_4\text{Cl}$ Admixture

A series of 30-minute burns, similar to those described in the November 1978-January 1979 quarterly report, were carried out using the same mineral/ $\text{MgCl}_2/\text{NH}_4\text{Cl}$ admixtures as shown in Table 3 of that report, but using a higher burn temperature (1100°C). The results are shown in Table 1.

It is clear that the increase in temperature resulted in a considerable improvement in alkali volatilization. The results may also have benefited from the use of a tube furnace and a flowing nitrogen atmosphere. In the case of the albite, about

two-thirds of the total alkali content was volatilized at 1100°C. Microcline lost more than 50% of its alkali content, and illite and montmorillonite also lost a considerable amount of alkali. It is notable that the muscovite did not lose much alkali under these conditions. This suggests that the muscovite structure is not readily substituted by Mg^{2+} ions. On the other hand, $CaCl_2/CaCO_3$ mixtures show a strong tendency to volatilize the alkalies from muscovite.

2.2 Burns with Carbon Additions

In order to determine the effects of reducing conditions on alkali volatility, mixtures of the pure minerals with $CaCO_3$ and $CaCl_2$, as used before, were further mixed with about 2% finely divided graphite, and burned in a nitrogen atmosphere for 30 minutes. The results of these burns are given in Table 2. (These results may be compared with the results shown in Table 1 of the quarterly report for February-April 1979.)

The evidence suggests that the effects of graphite additions increased alkali volatility slightly in all cases except that of the illite, compared to a nitrogen atmosphere alone.

2.3 Burns with $FeCl_3$ Additions

Previous alkali volatility results (February-April 1979), obtained using an atmosphere of $FeCl_3$, were not encouraging. It was decided, therefore, to try the effects of adding $FeCl_3 \cdot 6H_2O$ as an admixture with two of the pure minerals (albite and muscovite). The amount added in each case was such as to give a molar chloride:alkali ratio of 3, in order to allow for loss of HCl during heating.

The results of two sets of burns, in a nitrogen atmosphere for 30 minutes, at 900°C and at 1000°C, are given in Table 3. From these results, it is clear that only about 10-15% of the total alkali content was volatilized by this method. $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ is, therefore, much less effective than CaCl_2 or MgCl_2 as an admixture for increasing alkali volatility.

2.4 Effects of Increased Fineness

In order to determine the effects of particle size on alkali volatility, a sample of each of the "pure" minerals was ground so that at least 95% of the material passed a 325 mesh-sieve. These ultrafine minerals were mixed with CaCO_3 and $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ in the same proportions as used previously, and burned for 15 and 30 minutes at 1000°C in a flowing nitrogen atmosphere. The results are shown in Table 4, in comparison with previous data obtained on "normal" fineness materials.

It is apparent, from these results, that the differences in alkali loss between the ultrafine and the "normal" fineness minerals are small. In fact, in most cases, better alkali volatility was obtained using "normal" fineness material. This may be due to surface sintering. The results do show that much of the alkali loss occurs during the first fifteen minutes at 1000°C.

2.5 Effects of High Temperatures

Burns were made at 1300°C and 1450°C in air, for periods of 5 and 15 minutes, using mixtures of "normal" fineness minerals with CaCO_3 and $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ as used previously. Platinum boats were used, as in most cases the sample melted during the run.

The results are shown in Table 5; these may be compared with results in Table 4, and also with those in Table 1 of the quarterly report for November 1978-January 1979. These results indicate that some increase in alkali volatility can be obtained by heating to 1450°C , especially with the feldspars. However, it is also noticeable that the length of time at 1450°C has little effect on alkali loss, between 5 and 15 minutes. This is an important observation, because the time required for the volatilization step is a very important factor in the design of a reactor vessel. Moreover, it suggests that once the material melts to form a glassy liquid (of low specific surface), most of the alkali becomes trapped in the melt. Interestingly, the muscovite sample, which did not melt at 1300°C , lost more alkali at this lower temperature, which tends to confirm these conclusions.

2.6 Effects of Water Vapor

Burns were carried out in an atmosphere of nitrogen which had been saturated with water vapor at 50°C (giving 11% H_2O by volume). The ultrafine minerals were mixed with CaCl_2 and CaCO_3 , as used in Section 2.4. Results are shown in Table 6, and may be compared with those shown in Table 4.

It is apparent that, except for the feldspars, alkali volatilization was actually hindered by the presence of water vapor. This is a surprising result, since many sources have suggested that the opposite should be true. One possible explanation is that the reaction between CaCl_2 and H_2O , releasing HCl , may be more rapid than the volatilization of alkali chlorides, at these

temperatures, resulting in a depletion of chloride. This hypothesis will be tested by analyzing the reaction products for chloride content.

2.7 Effects of Reducing Atmospheres, With and Without Water Vapor

An atmosphere of natural gas (mainly CH_4) and dry nitrogen was used in the tube furnace, the flows being approximately 2 litres/minute N_2 and 0.26 litres/minute CH_4 . This atmosphere was used with and without saturation with water vapor at 52°C . At this temperature, the calculated water flow for the saturated gas mixture was approximately 0.3 litres/minute H_2O .

Experiments were conducted at 1000° and 1100°C for 30 minutes using ultrafine minerals plus CaCO_3 and CaCl_2 , as in Section 2.4. Results are shown in Table 7; these can be compared with the results discussed in Sections 2.4 and 2.6. It is interesting to note that the use of a reducing atmosphere improved alkali volatilization at 1000°C from the feldspars but not from the other minerals. Methane increased alkali volatilization in all cases compared to the effects of water vapor, but not compared to the effects of a pure nitrogen atmosphere. The combined effects of methane and water vapor together, at 1100°C , were generally disappointing. In all cases but one (albite), the alkali volatility decreased or remained the same within the limits of experimental error. This again suggests that water vapor actually removes the chlorine from the sample before it has a chance to react with the alkalies.

The situation regarding reducing conditions is somewhat confusing when the results for N_2 with CH_4 are compared to those for N_2 alone (Table 4). Both feldspars (albite and microcline) showed increased alkali volatilization in the presence of methane; but muscovite, montmorillonite, kaolin, and illite did not. Better results were achieved with solid graphite added to the sample (Table 2).

3. Alkali Volatility Studies on Typical Raw Feed Minerals (Task IV)

Work on this (Task IV) has been slow, due to difficulty in obtaining samples of suitable raw materials. We now have a total of eight minerals, including three shales, two fly ashes, and three clays. The analyses for the first four were given in the previous quarterly report. Analyses for the last four are given here, in Table 8.

Work in Task IV will continue. However, we feel at present that it is of more use to carry out the Task III work in more detail (see attached letter), and have therefore not yet conducted any further burns with the "typical" minerals. It seems to us that more can be done to optimize alkali volatilization by working on the "pure" minerals, and trying to fully characterize their behaviors rather than by carrying out an inordinately detailed series of tests on the "typical" minerals at this stage of the project.

Table 1: Burns of Pure Minerals with $\text{MgCl}_2/\text{NH}_4\text{Cl}$

Temperature = 1100°C
Sample size = 1.4-4.2 grams

Atmosphere = dry nitrogen flowing at approximately 2 l/min.
Duration = 30 minutes

Mineral	Weight of $\text{MgCl}_2/\text{NH}_4\text{Cl}$ added, per 100 units of mineral	Observed L.O.I., %	Alkali content, weight %, after burning at 1100°C		Alkali content, weight %, after burning at 1000°C*		
			Na_2O	K_2O	Na_2O	K_2O	
Kaolin PDC 155	0.804	15.50	0.07	0.14	0.13	0.20	Alkali loss is probably too small to be significant.
Albite PDC 156	64.52	41.88	4.17	0.35	7.06	0.70	Material sintered slightly at 1100°C. Considerable improvement in alkali volatilization at 1100°C.
Muscovite PDC 157	37.62	27.72	0.67	9.07	0.56	9.23	Little difference between 1000°C and 1100°C.
Montmorillonite PDC 158	12.25	27.10	1.75	0.64	2.32	0.88	This sample melted completely at 1100°C. Some improvement in alkali volatilization at 1100°C.
Microcline PDC 168	52.45	35.69	1.00	6.07	1.31	8.52	Considerable improvement in alkali volatilization at 1100°C.
Illite PDC 169	17.32	29.30	0.43	2.58	0.57	4.57	Considerable improvement in alkali volatilization at 1100°C. May be due to slightly reducing conditions, as well.

*These results were obtained earlier on thin-layer samples in a muffle furnace in an air atmosphere - see Table 3 of the quarterly report for November 1978-January 1979.

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Table 2: Burns of Pure Minerals with Graphite plus CaCl_2 and CaCO_3

Temperature = 1100°C

Atmosphere = dry nitrogen flowing at approximately 2 l/min

Sample size = 3-5.5 grams

Duration = 30 minutes

Mineral	Weight of additives intermixed, per 100 units of pure mineral			Observed Loss-on-ignition, %	Alkali content of product, weight %		Alkali content of original mixture, corrected for observed L.O.I.	
	CaCO_3	$\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$	Graphite		Na_2O	K_2O	Na_2O	K_2O
Kaolin PDC 155	20	0.35	2.5	19.22	0.09	0.12	0.05	0.13
Albite PDC 156	20	28.9	2.6	21.16	5.38	0.43	8.87	1.22
Muscovite PDC 157	20	17.5	2.5	23.29	0.35	4.20	0.61	8.85
Montmorillonite* PDC 158	20	5.5	2.3	21.75	1.48	0.43	1.96	0.54
Microcline PDC 168	20	23.5	2.5	18.42	1.20	7.13	1.70	9.41
Illite** PDC 169	20	17.6	2.6	22.06	0.38	1.81	0.53	3.87

*Chloride and total sulfur as SO_3 were determined on the product as 0.64% and 0.16%, respectively.

**Chloride and total sulfur as SO_3 were determined on the product as 0.76% and 0.87%, respectively.

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Table 3: Burns of Albite and Muscovite with Added $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$

Mineral	Albite	Muscovite
Weight of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ per 100 units of mineral:	106.3	64.3
<u>Alkali content of products</u>		
1) Burns at 900°C for 30 minutes in N_2		
% L.O.I.	26.32	28.07
% Na_2O	8.09	0.64
% K_2O	0.69	8.56
2) Burns at 1000°C for 30 minutes in N_2		
% L.O.I.	(26.5) *	28.27
% Na_2O	8.29	0.62
% K_2O	0.69	8.42
Calculated alkali content of product, if no alkali were volatilized during burn:		
% Na_2O	9.20	0.64
% K_2O	1.41	9.55

*Note: Estimated value

Table 4: Burns Made with Ultrafine Pure Minerals and CaCl₂/CaCO₃ Admixtures

Temperature = 1000°C Atmosphere = 2 l/min. dry N₂ Duration = 15 and 30 minutes
Pure minerals ground to -325 mesh before mixing with CaCl₂ and CaCO₃

Mineral	Weight of additives in mixture, per 100 units of pure mineral		Alkali content of product weight %				Alkali content of product* from 30 minute burn of normal fineness material	
			15 minute burn		30 minute burn			
	CaCO ₃	CaCl ₂ ·2H ₂ O	Na ₂ O	K ₂ O	Na ₂ O	K ₂ O	Na ₂ O	K ₂ O
Kaolin	20	0.35	0.04	0.12	0.04	0.10	--	--
Albite	20	28.9	6.6	0.83	5.8	0.66	6.10	0.67
Muscovite	20	17.5	0.38	5.2	0.31	4.1	0.32	3.10
Montmorillonite	20	5.5	1.93	0.53	1.85	0.48	(1.95)**	(0.57)**
Microcline	20	23.5	1.50	8.63	1.46	8.34	1.20	7.60
Illite	20	17.6	0.40	2.26	0.36	1.48	0.35	1.60

Notes: *Results from Table 1 of quarterly report, February-April 1979.
(Normal fineness raw materials with CaCO₃ and CaCl₂·2H₂O admixtures
in same ratio.)

**Results from muffle furnace burns, in an air atmosphere.

Table 5: High Temperature Burns of Pure Minerals with CaCl_2 and CaCO_3 * in Air

Mineral*	Alkali contents of products, weight %								Physical state of sample after run	
	Burns at 1300°C				Burns at 1450°C					
	5 minute burn		15 minute burn		5 minute burn		15 minute burn			
	Na ₂ O	K ₂ O	Na ₂ O	K ₂ O	Na ₂ O	K ₂ O	Na ₂ O	K ₂ O	At 1300°C	At 1450°C
Kaolin	0.05	0.12	0.05	0.12	0.04	0.16	0.04	0.13	Sintered	Melted
Albite	5.60	0.63	4.60	0.46	4.20	0.50	4.20	0.53	Melted	Melted
Muscovite	0.35	3.20	0.33	3.20	0.43	4.32	0.39	4.31	Sintered	Melted
Montmorillonite	2.00	0.57	2.00	0.55	1.89	0.56	1.89	0.54	Melted	Melted
Microcline	1.15	6.36	1.17	6.32	0.95	5.00	0.97	5.10	Melted	Melted
Illite	0.44	2.88	0.44	2.85	0.39	2.37	0.37	2.11	Melted	Melted

Note: *Mixtures of normal fineness material, with CaCO_3 and $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ in same proportions as shown in Table 4. Burn carried out in platinum boats in a current of atmospheric air.

Table 6: Ultrafine Pure Minerals Plus CaCO_3 and CaCl_2 ,
Burned in an $\text{N}_2/\text{H}_2\text{O}$ Atmosphere

Atmosphere: N_2 at 2 l/min saturated with water vapor at approx. 50°C (i.e., about 11% H_2O by volume)

Duration of burns: 30 minutes

Mixtures: Pure minerals ground to -325 mesh, mixed with $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ and CaCO_3 in the same proportions as indicated in Table 4.

Mineral	Burn temperature, $^\circ\text{C}$	Alkali content of products, weight percent	
		Na_2O	K_2O
Kaolin	1000	0.05	0.11
Kaolin	1200	0.04	0.12
Albite	1000	5.60	0.30
Albite	1100	4.70	0.32
Muscovite	1000	0.48	6.00
Montmorillonite	1000	2.00	0.29
Microcline	1000	1.41	7.20
Illite	1000	0.49	3.10

Table 7: Ultrafine Pure Minerals Plus CaCl_2 and CaCO_3 , Burned in a Reducing Atmosphere

Mixtures: As described in Tables 4 and 6

Duration of Burns: 30 minutes

Mineral	Burn Temperature, °C	Atmosphere*	Alkali content of products weight %		Comments
			Na_2O	K_2O	
Kaolin	1000	N_2/CH_4	0.04	0.11	An alumina boat was used
Kaolin	1000	N_2/CH_4	0.04	0.10	A graphite boat was used
Kaolin	1100	$\text{N}_2/\text{CH}_4/\text{H}_2\text{O}$	0.04	0.08	An alumina boat was used
Albite	1000	N_2/CH_4	4.60	0.39	An alumina boat was used
Albite	1000	N_2/CH_4	5.20	0.50	A graphite boat was used
Albite	1100	$\text{N}_2/\text{CH}_4/\text{H}_2\text{O}$	4.20	0.24	An alumina boat was used
Muscovite	1000	N_2/CH_4	0.39	5.10	An alumina boat was used
Muscovite	1100	$\text{N}_2/\text{CH}_4/\text{H}_2\text{O}$	0.39	5.50	An alumina boat was used
Montmorillonite	1000	N_2/CH_4	2.00	0.57	An alumina boat was used
Montmorillonite	1100	$\text{N}_2/\text{CH}_4/\text{H}_2\text{O}$	1.98	0.57	An alumina boat was used
Microcline	1000	N_2/CH_4	1.03	6.60	An alumina boat was used
Microcline	1100	$\text{N}_2/\text{CH}_4/\text{H}_2\text{O}$	1.29	7.40	An alumina boat was used
Illite	1000	N_2/CH_4	0.40	2.30	An alumina boat was used
Illite	1100	$\text{N}_2/\text{CH}_4/\text{H}_2\text{O}$	0.44	2.80	An alumina boat was used

*Note: N_2/CH_4 = approximately 2 l/min N_2 and 0.26 l/min CH_4
 $\text{N}_2/\text{CH}_4/\text{H}_2\text{O}$ = approximately 2 l/min N_2 , 0.26 l/min CH_4 , and 0.3 l/min $\text{H}_2\text{O}_{\text{vap}}$.

Table 8: Chemical Analyses of Typical Argillaceous
Raw Feed Components

Oxides, Weight %	Clay PDD 103 (Mineral #5)	Shale PDD 108 (Mineral #6)	Fly Ash 29612 (Mineral #7)	Clay PDD 118 (Mineral #8)
SiO ₂	51.5	31.6	52.6	54.4
Al ₂ O ₃	16.6	6.70	24.0	17.6
Fe ₂ O ₃	6.20	2.70	9.8	5.32
CaO	3.50	28.3	1.2	3.63
MgO	3.14	1.92	1.3	2.67
SO ₃ *	0.06	1.88	0.3	0.99
Na ₂ O	0.60	0.40	0.37	0.23
K ₂ O	2.41	1.44	3.19	5.10
P ₂ O ₅	0.131	0.093	ND	0.105
TiO ₂	0.73	0.33	ND	0.90
Mn ₂ O ₃	0.07	0.06	ND	0.05
Cl ⁻	0.006	0.003	ND	0.003
F ⁻	0.067	0.068	ND	0.111
L.O.I.	14.68	24.88	4.3	8.93
Total	99.69	100.37	96.76	100.52

Notes: *Total sulfur as SO₃, by Leco

ND = not determined