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
Feb. 1979 - April 1979

Submitted by
Ellis M. Gartner

Portland Cement Association
Construction Technology Laboratories
5420 Old Orchard Road
Skokie, Illinois 60077

May 1979

NOTICE
This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Department of Energy, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

Quarterly Technical Progress Report
February-April 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
Ellis Gartner

1. Summary

This report deals with laboratory tests designed to evaluate the volatility of alkalies in finely-ground argillaceous minerals. The final part of the report covers a method used to determine the sintering points of these minerals.

In addition to the six pure minerals which were studied during the first six months of this contract, we have now begun to study argillaceous materials which are more typical of cement-plant raw feed components.

The major conclusions of this report are as follows:

1. At 1000°C, a combination of CaCO_3 and CaCl_2 additives enables us to volatilize in one-half hour up to about 50% of the total alkali from high-alkali feldspars. However, much less alkali was lost from the "typical" cement plant raw materials under the same conditions.
2. The atmosphere in which the experiment is conducted may have a significant effect on the results, especially if there is sulfur present in the system. Absence of oxygen can lead to decomposition of normally involatile alkali sulfates.

3. Other volatile components, in particular iron chlorides, may be lost from the sample. Losses of FeCl_3 are likely to be greatest in the absence of CaO and water vapor.
4. The sintering points of the "pure" minerals are all above 1200°C . Therefore, there is little danger of their sintering at 1000°C , although the presence of "fluxing" agents such as CaCl_2 may cause some sticking.
5. The use of vapor-phase chlorine-containing compounds such as FeCl_3 and HCl is not an effective means of volatilizing alkalis under our test conditions (1000°C for 30 minutes).

Concurrent with the experimental work, we have continued at a low level with our literature study; two German papers have been translated and are now available to us in English. We will summarize this literature work at the end of the research program.

2. Alkali Volatilization Studies

2.1 $\text{CaCl}_2/\text{CaCO}_3$ Admixtures

We have now begun to use our new high-temperature tube furnace for alkali volatilization studies. This has enabled us to control the furnace atmosphere much more precisely than before. We have rerun the four high-alkali raw materials, mixed with CaCO_3 and CaCl_2 , in this furnace at 1000°C for 30 minutes, in a current of dry nitrogen. The results are given in Table 1, together with comparable results for the same mixtures run pre-

viously (taken from Table 1 of the November-January quarterly report).

From these results, it appears that the overall efficiency of alkali volatilization using the tube furnace with a nitrogen atmosphere is similar to that obtained using a large muffle furnace and an air atmosphere for the two feldspars (microcline and albite), although there are signs that the volatility of the potassium was decreased, and that of the sodium increased, by using a dry nitrogen atmosphere. This effect may also be influenced by the volatility of other components in the minerals. For example, there was evidence that small amounts of iron vaporized from all the minerals during the runs, presumably in the form of FeCl_3 . The sides of the alumina boats used to hold the samples were blackened during the runs, probably due to redeposition of iron oxide from the vapor phase, in the presence of traces of water vapor or oxygen.

As for the muscovite and illite samples, both showed a marked increase in alkali loss in the tube-furnace runs, as compared to the muffle furnace runs. The absence of oxygen may have had a large effect on the illite because of its high sulfur content; there is sufficient SO_3 in the illite to keep three-quarters of the K_2O in the solid as K_2SO_4 . In a nitrogen atmosphere, the decomposition of the illite may well lead to loss of sulfur as SO_2 , which in turn may decrease the amount of alkali sulfate and allow the more volatile alkali oxides and chlorides to form. However, this reasoning cannot explain the increase in alkali volatility for the muscovite, which contains

no sulfur. Possibly we are seeing the effects of the cross-contamination of samples which tended to occur when the muffle-furnace was used, because three samples were usually run simultaneously.

2.2 HCl Atmospheres

In order to generate an atmosphere of HCl in which to immerse the mineral samples at high temperatures, it was necessary to evaporate ammonium chloride (NH_4Cl) upstream of the sample; NH_4Cl dissociates into NH_3 and HCl vapors. The concentration of HCl in the atmosphere could then be back-calculated once the amount of NH_4Cl lost in a given time period was known. The carrier gas was either dry nitrogen or atmospheric air, i.e., respectively, mildly reducing (due to NH_3 vapor) or oxidizing (due to O_2 in excess of the NH_3 vapor). The results of nine test runs are given in Table 2.

It is apparent that very little alkali was volatilized by this method, even when (as in the case of the montmorillonite, for example) the amount of HCl vapor greatly exceeded the amount required to convert all the alkalies in the sample to their respective chlorides. The use of nitrogen atmospheres instead of air did not have any significant effect on the results.

2.3 FeCl_3 Atmospheres

An FeCl_3 atmosphere (in a carrier of dry N_2) was generated by evaporating FeCl_3 upstream of the sample. Due to the corrosive nature of FeCl_3 this was somewhat hazardous and ultimately led to the failure of the furnace tube. The results of two runs are given in Table 3.

It is clear from these results that the two minerals did not lose much of their alkali content, but they did gain a large amount of Fe_2O_3 . However, the minerals lost some weight during the run. At present, it is not clear what element was lost in order to make up for the gain in weight due to Fe_2O_3 . We plan to investigate this further. Nevertheless, it is disappointing to note that very little alkali was volatilized during these runs.

3. Alkali Volatilization from "Typical" Cement Raw Materials

We have now obtained four "typical" high-alkali argillaceous raw-feed minerals from various cement plants. The chemical analyses of the these four minerals are given in Table 4; X-ray diffraction analyses of the minerals are given in Table 5. It should be noted that the Anthrim shale is an oil shale and thus most of its sulfur will be in the form of organic or pyritic sulfides; this accounts for its high oxide total in Table 4. Although these minerals are considered high in alkali for cement raw feeds, they generally contain less alkalies than the feldspars and muscovite which were examined in the previous phase of the work. It is notable that the A-150 shale is high in potassium; this is accounted for by its high muscovite content, as shown in Table 5.

Table 5 also shows that the Durkee clay and the fly ash (21469) are probably more suitable as cement raw-feed components than are the two shales. This is because the glassy phases (in the fly ash) and the clay minerals (in the Durkee clay) are generally more reactive in cement raw mixes than the micas, quartz, illites and chlorites which make up the shales.

3.1 Alkali Volatilization Using CaCO_3 and CaCl_2

Since the combination of CaCO_3 and CaCl_2 was the most effective admixture for alkali volatilization in the case of the "pure" minerals, this admixture was tried first. Results of these tests as well as results of simple ignition runs at 1000°C are given in Table 6.

It is clear that very little alkali is lost from any of the samples simply by igniting them at 1000°C in air for 30 minutes. It is noticeable that the addition of CaCO_3 plus CaCl_2 greatly increases the alkali volatility. However, the percentage of alkali loss nowhere exceeds 22%, which is disappointingly low compared to the levels of alkali loss obtained with the high-alkali pure minerals under similar conditions (see Table 1).

4. Determination of Sintering Temperatures

In order to determine the sintering temperatures of the various minerals, it was necessary to devise a new test. We decided to use ASTM test method D1857-68, which is actually designed for the determination of the fusibility of coal ashes. This test consists of observing the deformation of miniature ($3/4$ in.) pyramids pressed out of the powdered mineral, when subjected to high temperatures. The temperature at which the first "rounding" of the apex of the pyramid occurs is referred to as the "Initial Deformation Temperature" (I.T.). The temperature at which the pyramid collapses into a rounded lump of height equal to basal width is referred to as the "Softening Temperature" (S.T.).

The pyramids were prepared by mixing the powdered minerals into a stiff paste with aqueous gum arabic, (3.95 grams/ml). The paste was molded in brass molds (see ASTM D1857), and the resulting pyramids were placed into a muffle furnace on a platinum sheet. They were heated in an air atmosphere at about 150°F/hr from 1400°F to 2450°F , and their temperatures were monitored, using an Optical pyrometer, to within $\pm 20^{\circ}\text{F}$. The results are given in Table 7.

It is notable that the kaolin and muscovite did not show any signs of sintering or melting below the maximum temperature at which we were able to make measurements. Of the others, the albite and illite softened at the lowest temperature; however, in all cases this temperature was above 1200°C and, therefore, well above the temperatures at which alkali volatilization runs were made.

The definition of the term "sintering point" is rather vague. The use, instead, of the "Initial Deformation Temperature," as defined above, seems reasonable. It is clearly desirable that any alkali volatilization technique which is to be carried out on a gaseous suspension of particles be run at a temperature below that at which the solids can sinter together, i.e., well below 1200°C . However, the addition of admixtures such as CaCl_2 is certain to produce small amounts of liquid phase at much lower temperatures than this. This may result in "sticking" of solid particles at temperatures as low as 700°C .

TABLE 1
Volatilization of Alkalies Using CaCO₃ and CaCl₂

Mineral, (to which 20% extra CaCO ₃ was added) ³	Approximate Weight of CaCl ₂ ·2H ₂ O added, per 100 units of Pure Mineral	Initial Alkali Content of Mix, Corrected for L.O.I. at 1000°C, % as Oxides		1000°C Thin Layer Burn, in Large Furnace, 1/2 hr (from Nov.-Jan. 1979 Quarterly Report, Table 1), % as Oxides		Total Alkali Loss, %, Relative to Original Alkali Content	1000°C Thin Layer in Alumina Boat in Tube Furnace, 1/2 hr, under Dry N ₂ at about 2 /min. % as Oxides		Total Alkali Loss, %, Relative to Original Alkali Content
		Na ₂ O	K ₂ O	Na ₂ O	K ₂ O		Na ₂ O	K ₂ O	
Microcline	23.5	1.83	10.09	1.17	6.87	32.6	1.20	7.60	26.2
Albite	28.9	9.12	1.25	6.49	0.55	32.1	6.10	0.67	34.7
Muscovite	17.5	0.63	9.19	0.46	4.85	45.9	0.32	3.10	65.2
Illite	7.8	0.54	3.95	0.43	3.04	22.7	0.35	1.60	56.6

TABLE 2

Volatilization of Alkalies by Heating in the Presence of HCl*

	Weight Loss on Heating in NH ₄ Cl Vapor, %	Atmosphere (neglecting NH ₃)*	Minutes at 1000°C	% Alkali in Original Sample, Corrected for observed L.O.I.		% Alkali After Heating in NH ₄ Cl Vapor		Moles of HCl Passed Over Sample During Run	Moles of Na and K in Original Sample	Initial Weight of Sample, grams
				Na ₂ O	K ₂ O	Na ₂ O	K ₂ O			
Albite	2.75	3.3% HCl/air	38	11.38	1.76	10.56	1.40	0.0326	0.0215	5.4686
Illite Shale	12.94	6.1% HCl/air	25	0.74	4.59	0.58	4.64	0.0420	0.0068	6.4380
Kaolin	14.40	14.2% HCl/air	30	0.07	0.15	0.05	0.15	0.1240	0.0002	4.6669
Kaolin	14.28	3.4% HCl/N ₂	30	0.07	0.15	0.04	0.16	0.0864	0.0002	4.4208
Microcline	1.33	2% HCl/N ₂	30	2.18	11.96	2.20	11.94	0.0396	0.0261	8.1663
Microcline	0.70	5% HCl/air	30	2.17	11.88	2.17	11.92	0.0371	0.0243	7.6115
Montmorillonite	18.71 ^A	5.4% HCl/air	40	2.37**	0.69**	2.42	0.75	0.0570	0.0035	4.7690
Montmorillonite	15.99	15% HCl/air	30	2.30	0.67	2.34	0.69	0.1330	0.0028	3.8004
Muscovite	5.30	13.6% HCl/air	30	0.70	10.35	0.65	10.32	0.1170	0.0168	7.3170

Notes: *Atmosphere generated by evaporating NH₄Cl upstream of sample. Concentration of HCl calculated by loss in weight of NH₄Cl, assuming
 $\text{NH}_4\text{Cl} \rightarrow \text{NH}_3 + \text{HCl}$.

** - Inaccurate due to some loss of sample

TABLE 3

Volatilization of Alkalies in an Atmosphere of FeCl_3 and N_2

<u>Mineral</u>	<u>Albite</u>	<u>Microcline</u>
Initial Weight of Sample, grams	8.0352	3.2535
Time at 1000°C in FeCl_3/N_2 Atmosphere, minutes	30	14
Loss on Ignition During Run, %	2.46	0.77
Weight of FeCl_3 Vaporized During Run, grams	5.9402	(about 3)*
Moles of FeCl_3 Vaporized	0.0366	(about 0.02)*
Total Molar Quantity of Na + K in Mineral	0.0316	0.0104
Approximate Volume Percent FeCl_3 in Atmosphere During Run; (Carrier gas was N_2 at 2 litres/ minute)	1.5	(about 1.5)*
<u>Partial Oxide Analysis of Product, %</u>		
Fe_2O_3	18.41	14.05
Na_2O	10.08	2.12
K_2O	1.05	11.42
<u>Partial Oxide Analysis of Unignited Minerals, %</u>		
Fe_2O_3	1.00	0.81
Na_2O	11.07	2.15
K_2O	1.71	11.80
L.O.I.	1.76	0.52

*Note: The second run was incomplete due to breaking of the furnace tube after 14 minutes.

TABLE 4

Chemical Analyses of Typical Argillaceous Feed Components

<u>Oxides, % by Weight</u>	<u>Anthrim Shale (Oil Shale)</u>	<u>Shale (A-150)</u>	<u>Durkee Clay (PDC 49)</u>	<u>Fly Ash (21469)</u>
SiO ₂	54.65	61.42	61.80	53.20
Al ₂ O ₃	13.84	22.75	13.50	28.70
Fe ₂ O ₃	6.07	3.80	5.74	9.50
CaO	2.07	0.15	2.84	1.31
MgO	2.40	0.76	1.26	1.02
SO ₃	6.89	0.20	0.14	0.35
Na ₂ O	0.55	0.11	1.44	0.58
K ₂ O	3.51	8.20	1.77	3.11
TiO ₂	N.D.	0.90	0.80	1.60
Mn ₂ O ₃	N.D.	N.D.	N.D.	N.D.
P ₂ O ₅	N.D.	0.17	0.07	0.37
Cl ⁻	N.D.	N.D.	<0.01	N.D.
F ⁻	N.D.	N.D.	0.05	N.D.
L.O.I.	14.88	4.24	9.25	3.00
Total	104.86	102.70	98.66	102.74

Note: N.D. = not determined

CR-7574-4330
May 1979

TABLE 5

Results of X-Ray Diffraction Analyses of
Four Argillaceous Raw Materials

Material	Minerals Observed by XRD	Comments
Anthrim Shale	Mainly quartz, chlorite, illite, mica and pyrite. Some pigeonite and traces of feldspar.	A poor quality shale for cement manufacture (mainly micaceous clay minerals). Most of the sulfur is in the reduced form (as iron pyrites).
Shale A-150	Mainly muscovite and quartz, some chlorite, olivine and titanate (sphene). Other minerals detected were feldspars, wustite, chloro-fluoro-apatite, phillipsite.	Poor quality shale for cement manufacture. Mainly mica and quartz. Very few clay minerals. High potash content due primarily to muscovite.
Durkee Clay	Mainly quartz plus poorly-crystalline montmorillonites, illites, and kaolinites. Appreciable amounts of plagioclase feldspars. Traces of calcite, amphiboles, and margarite or laumontite.	Reasonably high grade clay, but with a lot of quartz. Fairly high levels of illites and feldspars probably account for high alkali content.
Fly Ash 21469	Mainly mullite plus a glassy phase. Some quartz, magnetite and hematite. (Some unidentified broad peaks).	Partly crystalline, low-lime fly ash. The alkali may be mainly in the glassy phase.

TABLE 6

Alkali Volatilization from "Typical" Argillaceous Raw Materials*

	Calculated Alkali Content of Raw Material, on Ignited Basis, %		Alkali Content of Material After Ignition at 1000°C for 1/2 hour, in air		Weight of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ Added to 100 parts of Mineral plus 20 parts CaCO_3	L.O.I. of Mineral/ $\text{CaCO}_3/\text{CaCl}_2$ Mixture at 1000°C for 1/2 hour, in air	Alkali Content of Mixture After 1000°C for 1/2 hour, in air		Calculated Alkali Content of Ignited Mixture if no Alkali had Volatilized, %		Percentage of Alkali Volatilized by $\text{CaCl}_2/\text{CaCO}_3$ at 1000°C 1/2 hour, in air	
	Na_2O	K_2O	Na_2O	K_2O			Na_2O	K_2O	Na_2O	K_2O	Na_2O	K_2O
#1 Antrim Shale (Oil Shale)	0.65	4.12	0.61	4.10	7.872	22.63	0.49	2.80	0.56	3.55	12.5	21.1
#2 Shale A-150	0.11	8.56	0.10	8.50	14.296	17.29	0.08	5.80	0.10	7.38	20.0	21.4
#3 Durkee Clay	1.59	1.95	1.58	1.90	7.946	18.43	1.32	1.45	1.38	1.70	4.3	14.7
#4 Fly Ash 21469	0.60	3.21	0.60	3.13	7.941	13.88	0.49	2.20	0.53	2.82	7.5	22.0

*Note: All burns were made on "thin layer" sample, i.e., samples spread evenly over the base of a 50-mm diameter platinum dish, to a depth of about 2 mm. The ignition was carried out in a muffle furnace in an air atmosphere.

TABLE 7

Sintering Behavior of the Six "Pure" Minerals

Code Number	Mineral	Initial Deformation Temperature		Softening Tempertaure	
		°F	°C	°F	°C
PDC 155	Kaolin	>2450	>1343	>2450	>1343
PDC 156	Albite	2220	1216	2250	1232
PDC 157	Muscovite	>2450	>1343	>2450	>1343
PDC 158	Montmorillonite	2360	1293	2420	1327
PDC 168	Microcline	2370	1299	2470	1354
PDC 169	Illite	2235	1224	2245	1229