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Use of Precalciners
to Remove Alkali from Raw Material
in the Cement Industry
Progress Report
August-September-October 1978

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MASTER

Submitted by

F. MacGregor Miller

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

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Quarterly Technical Progress Report,
August-September-October 1978
Use of Precalciners to Remove Alkali from Raw Material
in the Cement Industry
DOE Contract - EM-78-C-02-4929
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F. M. Miller
Portland Cement Association
Skokie, Illinois 60077
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Summary

Attached are reports dealing with the results of: (1) a literature survey on the general topics of alkali volatilization and thermal treatment of raw materials, (2) a series of high temperature burns of selected ground argillaceous minerals, both with and without calcium chloride addition.

It was found that relatively little work has been published dealing with the specific question of vaporizing alkalies from raw materials external to the kiln. The literature survey was of use; however, in defining the role of CaCl_2 and limitations on its applicability to alkali reduction experimentation. Additional insight into the mechanism and parameters of heat exchange in the precalciner-type kiln systems has been gained from the literature search, which culminated in the preparation of the bibliography covering thermal treatment of raw materials. Further discussion of these results of this literature survey will be given in our next quarterly report.

The experiments investigating the efficiency of alkali volatilization from pure argillaceous minerals are well underway. Initial results have been encouraging, as significant

fractions of total alkali were volatilized even under the static conditions employed. Clay minerals were, rather surprisingly, more resistant to alkali removal than feldspars when CaCl_2 was used. This may indicate that their structure collapsed upon removal of some alkali, and that CaCO_3 should be added to the clay burns (as outlined in Item III.C-5 of the work program).

In addition to evaluating the effect of CaCO_3 additions with the clays, we plan to determine sintering points for the minerals and to try FeCl_3 as an additive for alkali volatilization. Despite its volatility, FeCl_3 is an attractive candidate because of its low cost (much FeCl_3 is a waste product of metal "pickling"). Further work will be carried out to test the effects of fineness, sulfur, and pyroprocessing atmosphere on the efficiency of alkali volatilization.

Precalciner Project: Literature Study

The literature survey was begun with the production of two PCA library bibliographies,* one covering "Alkali Beneficiation of Raw Materials"⁽¹⁾ and the other dealing with "General Heat Exchange and Thermal Treatment of Raw Materials, with Emphasis on Precalcining."⁽²⁾ We are now in the process of checking through the approximately 120 articles and patents which are included in these bibliographies. In the alkali beneficiation category, the majority of papers deal with methods of reducing the alkali content of clinkers from existing kiln systems, and we have not yet come across any papers dealing with alkali volatilization from specific raw feed components. However, there are some useful points that can be deduced from the papers covered so far. Several papers mention the effectiveness of CaCl_2 in inducing alkali volatilization in the kiln. Bohman⁽³⁾ found that an 0.2% addition of CaCl_2 to the raw feed in a suspension preheater kiln decreased clinker K_2O from 1.7% to 1.5% (the bypass gas fraction was simultaneously increased from 5% to 7%). The decrease in clinker K_2O was almost exactly equal to the expected decrease on the assumption that all the CaCl_2 was converted to KCl , which could be removed from the system (in the bypass dust).

An earlier paper by Nordquist and Heian⁽⁴⁾ dealt with the use of CaCl_2 additions via the fuel burner pipe of a gas-fired, grate-preheater kiln. They used higher addition rates

*Note: Copies of these bibliographies are included in this report as Appendices I and II.

than in Reference 3; typically about 0.8% CaCl_2 relative to clinker production. However, the total alkali content of the clinker fell from about 0.73% when operating with bypass and no CaCl_2 to about 0.55% when operating with bypass and 0.66% CaCl_2 . This amount of CaCl_2 should be equivalent to 0.49% K_2O in the clinker, so clearly much of the added CaCl_2 was ineffective in volatilizing clinker alkali. In fact, almost the same degree of alkali removal was brought about by adding only 0.28% CaCl_2 relative to clinker. Thus there is apparently a limit to the amount of alkali which can be volatilized by CaCl_2 with the raw materials and kiln type studied. However, the degree of volatilization in this case could also have been affected by loss of the CaCl_2 in the bypass dust.

One point which clearly emerges from all the references examined so far is that a considerable amount of the kiln exit gases must bypass the preheater when high-alkali, -sulfur and -chloride contents occur in the kiln feed (and fuel). Two papers^(5,6) point out the considerable advantage that precalciner kilns have in this respect; namely, that up to 100% of the kiln gases can be bypassed, without a drastic loss of fuel efficiency. Biege and Parsons⁽⁵⁾ claim that the "SF" flash calciner kiln can produce clinker at 0.42% total alkali with 100% bypass, with an energy requirement of 936 kcal/kg, using a high alkali raw material which would give 1.03% alkali in the clinker in a zero bypass system. (The energy requirement at zero bypass would be 750 kcal/kg).

This points out the potential for further improvement obtainable with the proposed "separate argillaceous precalciner" kiln, where it is hoped that a Btu loss equivalent to considerably less than 100% of bypass kiln exit gases will be required to obtain equivalent alkali reductions.

References

1. PCA Limited Bibliography No. 222, "Alkali Beneficiation of Cement Raw Materials," (1945-1978), October 3, 1978.
2. PCA Limited Bibliography No. 221, "General Heat Exchange and Thermal Treatment of Raw Materials, with Emphasis on Precalcining," (1940-1978), October 3, 1978.
3. Bohman, R., "Effect of the Addition of Calcium Chloride to the Kiln Feed Meal on the Alkali Balance and Clinker Quality of Preheater Kilns," Zement-Kalk-Gips 31 (6), pp. 278-281, June 1978.
4. Nordquist, E.A. and Heian, G.A., "Alkali Removal via the Grate Kiln System," Rock Products 76 (5), pp. 60-64, 179, May 1973.
5. Biege, N.W. and Parsons, L.J., "Bypass Systems for Preheater and Flash Calciner Kilns," Pit and Quarry, pp. 91-97, July 1978.
6. Svendsen, J., "Low-Alkali Cement from High-Alkali Raw Materials with Energy-Saving Process Technology," Zement-Kalk-Gips 31 (6), pp. 281-284, June 1978.

Use of Precalciner Project

Status of Experimental Work, November 13, 1978

General Description

Work has proceeded with analyses and burning tests on six pure minerals, representing the types of argillaceous minerals which are predominant in cement kiln feeds. Samples of the six minerals, (plus two further minerals as reserve samples) were received in lump form; these were ground to typical raw-feed fineness in a disc pulverizer mill. The sieve analyses for the ground materials are given in Table 1. It should be noted that the mica (muscovite, PDC 157) was very difficult to grind due to its "flaky" nature; however, even though it appears somewhat coarse as judged by sieve analysis, it will still have a high specific surface area due to the laminar shape of the particles.

Representative samples of each of the raw materials were analyzed for content of major oxides using atomic absorption spectroscopy; the results are given in Table 2. The materials were examined qualitatively by powder x-ray diffraction, and the results are given in Table 3.

Samples of each of the six typical feed minerals were subjected to burning tests to determine the amount of alkali loss under various heating conditions, with and without additions of calcium chloride. The test method is described below.

Static Vaporization Test Method

Two types of burning test were carried out, which we will refer to as thin-layer (TL) and pellet (P). In the thin-layer

burns, the powdered material was placed in a layer approximately 2-mm thick in the bottom of a 60-mm diameter platinum dish. In the pellet burns, the powder was pressed into pellets of about 10-mm height and 25-mm diameter, which were also placed in platinum dishes. The dishes containing the samples were placed directly into a large electric muffle furnace at the predesignated temperature. They were left in the furnace for 30 minutes, then withdrawn and allowed to cool in a desiccator. Each cooled sample was crushed and thoroughly homogenized, and a sample was analyzed for alkali content by flame photometry using a lithium metaborate fusion method to ensure complete dissolution of the sample in water.

Burns were carried out on each of the six raw materials alone at 900°C and 1000°C using the thin layer (TL) method. Mixtures of the raw materials with calcium chloride dihydrate ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$), in a quantity approximately equivalent to the alkali-oxide content on a molar basis, were burned at 900, 1000 and 1100°C in both thin layer (TLC) and pellet (PC) forms. Due to the extremely deliquescent nature of calcium chloride, it was necessary to mix each mineral with a solution of the chloride, to dry the material, and then to regrind it gently in a mortar and pestle. This assured good mixing and improved contact between alkali and chloride. The deliquescence problem also made it difficult to obtain accurate values of the loss on ignition of the mixtures during the runs.

The results of the burns carried out so far are given in Table 4. In this table, the amount of the original alkali

which was lost from the sample during the test is given as a percentage in Columns 6 and 7. These values were calculated on the assumption that the total weight of the sample remaining after the burn was as follows.

$$\text{Final weight} = W_o \left(1 - \frac{L}{100}\right) + 0.7549C - L_s$$

where W_o is the original weight of the pure mineral before ignition, L is the percentage loss on ignition of the pure mineral at 950°C , and C is the original weight of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ in the sample before ignition. The original weight of the sample before ignition, therefore, would have been $(W_o + C)$. L_s is the estimated weight loss due to alkali vaporization on the assumption that all the alkali was lost as chloride (NaCl or KCl). L_s could be estimated approximately from the final alkali content of the ignited sample, although in all cases it was a relatively small correction factor amounting to less than 5% of sample weight. The factor of $0.7549C$ accounts for loss of water from the calcium chloride. Due to the deliquescence of the calcium chloride, it was not possible to accurately determine the actual ignition losses during the runs, and the method of calculation described above probably give the best estimates of alkali loss which can be made from the experimental data.

Discussion of Results

In several cases, negative values were determined for the loss of alkali during the burn. This was especially true for the montmorillonite potassium content. Such results suggest that the experimental error is too high, in these specific

cases, to draw any conclusion as to true alkali loss, due to the low content of alkali in the original sample. However, the majority of the results were consistent and positive. The bracketed results in Table 4 are considered dubious.

1. PDC 155 Kaolin

This mineral had a very low initial alkali content, and would clearly be a very suitable component of cement kiln feed without requiring any means of alkali reduction. The results of the test burns are subject to a high probability of error due to the high loss on ignition and low alkali content of the pure mineral. Nevertheless, they generally show small losses of alkali under all conditions, but the scatter in the results is too great to draw any strong conclusions as to the effect of calcium chloride additions.

2. PDC 156 Albite

This material gave excellent results. There was very little loss of alkali during the thin layer burns without calcium chloride at 900°C or 1000°C, but, under the same conditions with calcium chloride, over 20% of the alkalies were driven off at 900°C, increasing to nearly 28% at 1100°C. The pellet burns gave somewhat lower losses of alkali, especially of the more abundant sodium. This trend would be expected due to the smaller surface-to-volume ratio of the pellets compared to the thin layer samples. With this material, fumes of alkali chloride could be seen emanating from the sample when the furnace was opened to withdraw the samples after burning. It is very likely that more alkali could have been removed by burning

for a longer period. This will be investigated in further tests.

3. PDC 157 Muscovite (Mica)

This material has a high potassium content, and the results clearly show significant losses of potassium which increase with increasing temperature. However, with the thin layer samples, there appears to be no benefit from addition of calcium chloride. Only pellets showed an increase in alkali loss in the presence of calcium chloride. It is difficult to explain these results other than to attribute them to the presence, in the mica, of some water, which may be retained even at high temperatures. The pellets might retain more water than the thin layer samples, and this water could catalyze the volatilization of alkalies at the higher temperatures, e.g., by bringing about the formation of KOH, which is more volatile than KCl.

4. PDC 158 Montmorillonite

Due to the high loss on ignition and relatively low alkali content of this material, the results were somewhat inconclusive. However, they do suggest that the addition of calcium chloride to the sample may increase the volatilization of the sodium.

5. PDC 168 Microcline

This was a typical high-potash feldspar which would require some alkali removal in order to be of use as a kiln feed component, especially in the manufacture of low-alkali cements. The material showed improved loss of alkali with increasing temperature and in the presence of CaCl_2 . Surprisingly, more

alkali was lost from the pellets than from the thin layer samples. In both cases the burns at 1100°C gave the best values for alkali loss.

6. PDC 169 Illite-Bearing Shale

This material would also be a typical component of many kiln feeds, and it does have a fairly high alkali content. The experimental results are interesting in that the samples without calcium chloride apparently lost at least as much alkali as the samples with calcium chloride, except in one case. There was also no clear trend with temperature. This suggests that loss of alkali may be related to the changes which occur in the structure of the illite when it is heated. It may then lose alkali as KOH and NaOH, if there is still some residual water in the structure at the high temperatures.

Generally, it appears that the feldspars and mica have so far responded best to the addition of calcium chloride and the use of high temperatures to drive off alkalies. This is encouraging, as these are the minerals which are usually most difficult to break down in the cement kiln under typical conditions. Further work will help to determine whether more alkali can be volatilized under different conditions. The illite has shown some moderately encouraging results. The results from the other clay minerals have been less conclusive. Longer burning periods should be tried on some of the samples, to determine whether the observed alkali losses represent equilibrium situations or whether the alkali losses are determined mainly by kinetics.

TABLE 1 - SIEVE ANALYSES ON GROUND MINERALS

<u>Lab. No.</u>	<u>Mineral</u>	<u>% Retained on 100 Mesh Sieve</u>	<u>% Passing 100 Mesh Sieve</u>	<u>% Passing 200 Mesh Sieve</u>
PDC 155	Kaolin	1	99	96
PDC 156	Albite	11	89	68
PDC 157	Mica	32	68	50
PDC 158	Montmorillonite	5	95	71
PDC 168	Microcline	7	93	72
PDC 169	Illite (Shale)	11	89	70
PDC 159	Anorthoclase*	1	99	74
PDC 160	Labradorite*	10	90	67

*Note: These two extra minerals were ground and analyzed, but were not used in the majority of the tests as they are perhaps less typical components of cement kiln feeds.

TABLE 2 - CHEMICAL ANALYSES OF PURE MINERALS

Mineral	Content of Major Oxides Expressed as Weight Percent*									Loss on Ignition, %
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃ *	Na ₂ O	K ₂ O	TiO ₂	
PDC 155, Kaolin	45.0	38.9	0.44	0.2	0.02	0.02	0.06	0.13	1.5	14.21
PDC 156 Albite	57.7	23.7	1.00	2.6	0.06	0.09	11.07	1.71	0.1	1.76
PDC 157 Muscovite (Mica)	46.7	31.0	5.11	0.3	1.02	0.00	0.686	10.16	0.4	5.33
PDC 158 Montmor- illonite	56.2	17.9	3.85	1.4	1.60	0.57	1.93	0.56	0.3	15.81
PDC 168 Microcline	65.8	17.4	0.81	0.7	0.04	0.08	2.15	11.80	0.06	0.52
PDC 169 Illite (Shale)	51.5	17.7	5.12	4.5	1.96	2.57	0.64	4.00	0.8	11.79

*Note: All analyses by atomic absorption, except for SO₃ which represents total sulfur determined by LECO furnace.

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TABLE 3 - RESULTS OF X-RAY DIFFRACTION EXAMINATIONS

<u>Mineral</u>	<u>Chemical Formula of "Ideal" pure mineral</u>	<u>Impurities detected by X-Ray Diffraction</u>	<u>Comments</u>
PDC 155 Kaolin	$\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O}$	None	This is an almost pure kaolinite with only traces of alkali
PDC 156 Albite	$\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$	Traces of illite and muscovite	This is a reasonably pure sodium feldspar
PDC 157 Muscovite (Mica)	$\text{K}_2\text{O} \cdot 3\text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2 \cdot 2\text{H}_2\text{O}$	None	Probable substitution of Fe^{+3} for Al^{+3} in lattice
PDC 158 Montmorillonite	$\text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2 \cdot n\text{H}_2\text{O}$	Traces of calcite and undecomposed feldspars	This is a partly substituted clay mineral with variable water content, which always contains some alkali, and usually magnesium and calcium
PDC 168 Microcline	$\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2$	Traces of labradorite, albite & quartz	This is a reasonably pure potassium feldspar
PDC 169 Illite	$3\text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2 \cdot \text{K}_2\text{O} \cdot 2\text{H}_2\text{O}$ (approximately)	Contains some quartz and albite	Illite is a name which covers a range of mica-like clay mineral compositions. This sample is a typical illite-bearing shale

TABLE 4 - RESULTS OF ALKALI VAPORIZATION TEST BURNS

Material	Conditions of Burn* Temperature °C	Weight of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ Added per Unit Weight of Mineral	Alkali Content of Product, % by Weight		Calculated Percentage of Original Alkali Content which was Vaporized During Burn		Properties of Pure Mineral Used in Test
			Na_2O	K_2O	Na_2O	K_2O	
PDC 155 <u>Kaolin</u>	900° TL	0	0.051	0.133	27.1	12.2	$\text{Na}_2\text{O} = 0.06\%$
	1000° TL	0	0.059	0.143	15.6	5.6	
	900° TLC	0.0067	0.060	0.160	13.7	(-6.2)	$\text{K}_2\text{O} = 0.13\%$
	1000° TLC	0.0067	0.055	0.135	20.9	10.4	
	900° PC	0.0067	0.048	0.134	31.0	11.0	L.O.I. at 950°C
	1000° PC	0.0067	0.055	0.148	20.9	1.8	= 14.21%
	1100° PC	0.0067	0.047	0.147	32.4	2.4	
PDC 156 <u>Albite</u>	900° TL	0	11.01	1.96	2.3	(-12.6)	$\text{Na}_2\text{O} = 11.07\%$
	1000° TL	0	11.25	1.59	0.2	8.7	
	900° TLC	0.219	7.99	1.05	19.7	31.6	$\text{K}_2\text{O} = 1.71\%$
	1000° TLC	0.219	7.80	(0.47)	22.1	(69.6)	
	1100° TLC	0.219	7.19	1.14	28.2	26.2	L.O.I. at 950°C
	900° PC	0.219	8.07	1.28	18.6	16.4	= 1.76%
	1000° PC	0.219	8.40	1.20	15.1	21.5	
PDC 157 <u>Mica</u>	900° TL	0	0.650	10.30	10.3	4.0	$\text{Na}_2\text{O} = 0.686\%$
	1000° TL	0	0.733	9.09	(-1.2)	15.3	
	900° TLC	0.128	0.625	9.50	5.8	3.3	$\text{K}_2\text{O} = 1.71\%$
	1000° TLC	0.128	0.630	8.70	5.8	12.1	
	1100° TLC	0.128	0.600	8.53	10.4	14.0	L.O.I. at 950°C
	900° PC	0.128	0.615	8.85	7.9	10.5	= 5.33%
	1000° PC	0.128	0.638	7.95	5.3	20.3	
	1100° PC	0.128	0.680	7.58	(-0.7)	24.2	

TABLE 4 - RESULTS OF ALKALI VAPORIZATION TEST BURNS
(Continued)

Material	Conditions of Burn* Temperature °C	Weight of CaCl ₂ ·2H ₂ O Added per Unit Weight of Mineral	Alkali Content of Product, % by Weight		Calculated Percentage of Original Alkali Content which was Vaporized During Burn		Properties of Pure Mineral Used in Test
			Na ₂ O	K ₂ O	Na ₂ O	K ₂ O	
PDC 158 <u>Montmor-</u> <u>illonite</u>	900° TL	0	2.27	0.560	1.0	15.8	Na ₂ O = 1.93%
	1000° TL	0	2.41	0.686	(-5.1)	(-3.1)	
	900° TLC	0.0415	2.20	0.695	0.5	(-8.4)	K ₂ O = 0.56%
	1000° TLC	0.0415	2.10	0.700	5.0	(-9.2)	
	1100° TLC	0.0415	2.30	0.675	(-4.1)	(-5.3)	L.O.I. at 950°C
	900° PC	0.0415	2.04	0.655	7.7	(-2.1)	= 15.81%
	1000° PC	0.0415	2.19	0.680	0.9	(-6.0)	
	1100° PC	0.0415	1.70	0.730	2.34	(-13.4)	
PDC 168 <u>Micro-</u> <u>cline</u>	900° TL	0	(2.90	4.70	-34.2	60.4)	Na ₂ O = 2.15%
	1000° TL	0	2.19	11.90	(-1.3	-0.3)	
	900° TLC	0.180	1.90	10.65	1.0	(-1.1)	K ₂ O = 11.80%
	1000° TLC	0.180	1.66	9.25	14.8	13.5	
	1100° TLC	0.180	1.68	7.67	15.1	29.3	L.O.I. at 950°C
	900° PC	0.180	1.78	10.20	7.8	3.7	= 0.52%
	1000° PC	0.180	1.68	9.05	14.0	15.5	
	1100° PC	0.180	1.40	6.76	30.0	38.4	
PDC 169 <u>Illite</u>	900° TL	0	0.587	3.88	19.0	14.4	Na ₂ O = 0.640%
	1000° TL	0	0.651	3.93	10.3	13.3	
	900° TLC	0.0602	0.570	4.15	17.7	4.1	K ₂ O = 4.00%
	1000° TLC	0.0602	0.610	3.45	12.5	20.8	
	1100° TLC	0.0602	0.637	4.02	8.1	7.2	L.O.I. at 950°C
	900° PC	0.0602	0.565	4.23	18.3	2.2	= 11.79%
	1000° PC	0.0602	0.635	4.35	8.1	(-0.8)	
	1100° PC	0.0602	0.627	3.76	9.7	13.4	

*Note: TL = thin layer, TLC = thin layer with CaCl₂, PC = pellet with CaCl₂.

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