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Report to
DEPARTMENT OF ENERGY
Washington, D.C.

Use of Precalciners
to Remove Alkali from Raw Materials
in the Cement Industry

Quarterly Technical Progress Report
November 1979-January 1980

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Use of Precalciners to Remove Alkalies from
Raw Materials in the Cement Industry

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by
Ellis Gartner
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1. Summary

Most of the work in this quarter has involved further experiments using the "sulfate fusion" technique. High degrees of alkali removal have been achieved using CaSO_4 admixtures with added CaCl_2 and $\text{Mg}(\text{NO}_3)_2$. The presence of Mg^{2+} or Cl^- in the mixtures did not affect the phase separation significantly.

There was considerable evidence for preferential migration of K^+ into the sulfate phase, relative to Na^+ . A new technique, the "powder drop" method, was used to attempt to more closely simulate the alkali removal reactions which would occur in a reactor. Rapid removal of K^+ from most minerals was shown to occur with a sulfate melt initially containing 20% Na_2SO_4 and 80% CaSO_4 . However, in most cases, the Na^+ content of the slag layer actually increased.

Discussions have been carried out with a possible subcontractor regarding the design and construction of a "continuous production" bench-scale reactor. The detailed designing of such a reactor will not be possible until the second phase of this research project.

2. Sulfate Fusion Tests

Most of the experimental work this quarter has been involved with determining the effectiveness of the "sulfate fusion" technique, which was first discussed in the previous quarterly report. Further experiments have been and are being carried out with the intention of expanding the range of conditions in an attempt (a) to remove the maximum amount of alkali from each mineral, (b) to determine the "degree of partition" of each alkali metal between the two melts, (c) to study the partition of other elements (S, Cl, Fe, Al, Ca) between the two melts, and (d) to determine the rate of alkali removal and melt separation.

X-ray diffraction analyses of both product layers have also been carried out, in some cases, to determine the nature of the solidified products.

2.1 Fusions with a Magnesium Nitrate Admixture

In previous tests, the two fly ashes (Minerals #4 and #7) had given rather poor results when fused with CaSO_4 alone. This was felt to be due to the presence of carbon in the fly ash which could reduce calcium sulfate to give SO_2 ; this could then remove the sulfate from the system:

In order to try and prevent this, a small amount of magnesium nitrate was added to the sulfate fusion mixture, with the double purpose of oxidizing any carbon and introducing MgO to determine its effect on the system. In one case (fly ash 29612) the fly ash was also pre-ignited at 1000°C in air to oxidize it.

The results are given in the first two rows of Table 1. Test P34 can be compared to test P28 in the previous quarterly report; it shows a slight improvement in alkali removal, which may be due either to oxidation or to MgO, or both. However, test P33 gave a considerably better result than the previous test (P31) with unignited fly ash 29612, in which no sulfate layer was formed. This indicates that oxidation by pre-ignition to burn off carbon and oxidize reduced iron compounds is probably advantageous if the raw material contains such compounds.

2.2 Fusions with a Calcium Chloride Admixture

One element which frequently causes problems in the operation of preheater kilns is chlorine. This is because it is very volatile (in the form of sodium or potassium chlorides), and tends to vaporize in the kiln and recondense in the preheater. Thus, concentration by a factor of 50 or more at the back end of the kiln is not uncommon; i.e., 0.02% Cl^- in the raw feed can lead to levels of the order of 1% Cl^- in the feed entering the kiln from the preheater or precalciner. These levels frequently cause operational problems, such as hard rings or buildups in the kiln or preheater.

One of the important functions of the "bypass" on a preheater or precalciner kiln is to remove chlorine from the kiln system at its point of greatest concentration, near the back end of the kiln. Any system which replaces a "bypass", such as the sulfate-fusion furnace discussed here, must also remove chlorine in order to prevent operating problems. It is known that the alkali chlorides (NaCl and KCl) dissolve in molten

sulfates, and it is very likely that most of the chlorine in the kiln feed would tend to leave the system with the sulfate melt. However, we felt it necessary to test this hypothesis, and also to determine whether high chloride levels would have any detrimental effect on the alkali-sulfate phase separation technique.

To this end, sulfate fusions were carried out in the normal way, but with the addition of a small amount of calcium chloride to the mixture. The initial Cl^-/SO_3 ratios of the fusion mixtures were 0.07 in every case. This is in the typical range of Cl^-/SO_3 ratios for a preheater kiln operating with a high-sulfur fuel. All of the fusion mixtures (except P38) were prepared and ignited in covered platinum crucible in an air atmosphere for 10 minutes at 1250°C . In no case did sufficient phase separation occur at 1250°C , so the temperature was increased to 1280°C and the samples reignited for 10 minutes. Several of these samples showed good separation after this heat treatment, and were removed for analysis. The remaining samples were heated to 1310°C for a further 10 minutes, and then gave good phase separation. Sample P38 only was heated at 1300°C for 10 minutes.

In most cases (except P43), it was reasonably easy to distinguish an upper and lower layer in the crucible, and to separate them at least partially by hand. The lower layer material was washed (in a coarse state) and then analyzed for Al_2O_3 , Na_2O , K_2O , SO_3 and Cl^- . Results are given in Table 1.

It can be seen, from the last three columns of the table, that reasonably good levels of alkali removal were obtained in most of the experiments, regardless of duration, temperature, and initial alkali content. Some materials with a fairly low initial alkali content, (e.g., fly ash 21469, Run P42) gave a surprisingly high alkali loss. It is likely that vaporization of KCl and NaCl during the tests accounted for some of this, although the "boiling points" of both of these salts are well over 1400°C. Clearly, the presence of chloride did not hinder the phase separation. It is also interesting to note that, in every case, a higher fraction of the potassium was removed from the raw material than the sodium. This was true even for the Durkee clay, which initially contained almost as much sodium as potassium. It suggests that the sulfate fusion method preferentially extracts potassium from the argillaceous feed materials.

The actual degree of alkali removal from the slag, i.e., the true alkali/alumina ratio (N/A) of the slag, is dependent on whether we assume that the sulfate and chloride found in the lower layer by chemical analysis are present in solid solution, or in the form of alkali and/or calcium sulfates dispersed throughout the medium. X-ray diffraction studies (see Section 2.4) indicate that at least some alkali and calcium sulfates do remain mechanically trapped in the lower layers. Therefore, the true degree of alkali removal cannot be determined accurately. However, in order to give definite limits to this factor, we have calculated the final alkali/alumina ratio of the slag on two bases. The normal ratio (N/A) assumes all of

the alkali present in the lower layer is chemically a part of the slag. The "corrected" value of N/A assumes that all of the sulfate and chloride in the lower layer is combined preferentially as alkali sulfates or chlorides. Thus, the true value of N/A will fall between these two limits. In most cases, this suggests that the true degree of alkali removal may be well above the values given, as "uncorrected" values, in the last three columns of Table 1.

It is also of interest to note the wide variation of chloride contents for the slag layer. In most cases, the chloride level indicates that the majority of the chloride is either in the sulfate layer or has evaporated, but in some cases (P35, P42, etc.) this is not the case. In all of these cases, however, the "corrected" N/A value is negative. This suggests that chloride probably combines preferentially with Na^+ or K^+ and dissolves in the sulfate layer, but if there is excess chloride trapped in the slag as CaCl_2 , it dissolves in the slag itself. Further studies of chloride partitioning will be required if this conclusion is to be confirmed.

2.3 "Powder Drop" Fusion Tests

In the proposed design of a sulfate fusion reactor, preheated alkali-rich raw feed will fall, under gravity, into a molten layer of mixed alkali and calcium sulfates. The material should then melt to form a low-alkali slag which will sink to the bottom of the sulfate layer and be tapped off.

In order to test this method under more realistic conditions than the "sulfate fusion" technique used previously, we

developed a method which we will refer to as the "powder drop" method.

In this test, a molten sulfate liquid was produced initially by melting a mixture of 80% CaSO_4 :20% Na_2SO_4 in a platinum crucible in a muffle furnace at 1300°C . Small amounts (0.2-0.5 grams) of the powdered raw material (typical finenesses approximately 70-80% -200 mesh) were then dropped into the melt from above. The furnace door was shut for a few minutes until the temperature reached 1300°C , and then the "powder drop" was repeated. This was continued for 20-30 minutes. Finally, the crucible was withdrawn from the furnace and quenched, as before.

The results of these tests were very interesting. In virtually every case, two layers were formed, with the lower layer being the "slag" layer, as expected. Due to the large amount of sulfate relative to raw material used in these tests, fairly large amounts of sulfate remained at the end of the tests. In some cases, surface tension effects produced "rings" of slag around the walls of the crucible, with a hole in the middle. However, it was evident that in some cases, the slag was denser than the sulfate melt, although in the case of microcline (test P45), it was difficult to distinguish the two layers, as they were almost identical in color.

The lower layers (slag layers) from each test were analyzed for Al_2O_3 , SO_3 , Na_2O and K_2O . Results are given in Table 2. Clearly, the sample from the microcline test was actually the sulfate layer, as it was rich in alkali and poor in Al_2O_3 .

All of the others were slags. The alkali content of the slag layer was calculated both with and without correction for sulfate in Table 1. However, in this case it was assumed that, in the "corrected" values, all of the trapped alkali sulfate would be present as Na_2SO_4 . Thus, only the Na_2O - contents are corrected.

The results all show considerable similarities. The most significant finding is the difference in behavior of sodium and potassium. In all cases except that of albite, sodium was actually taken up by the slag, whereas the potassium content of the slag decreased by a large amount. This led to an overall increase in alkali content of the slag (on an uncorrected basis) in all but two cases. The corrected values showed overall decreases in all cases except for montmorillonite. The uptake of sodium was lowest in those samples with a high initial sodium content, especially albite. Moreover, the fractional potassium losses in all cases were very high compared to results obtained by the standard calcium sulfate fusion method. The preferential migration of K^+ to the sulfate melt is probably due to its large ionic radius.

The results are encouraging for the following reasons:

1. Most high-alkali argillaceous raw materials found in the U.S. are rich in potassium.
2. The sodium levels used in the sulfate layer used for these fusions were much higher than those that are likely to occur in practice, and this tends to exaggerate the sodium partition effects.

3. Preferential removal of potassium from the raw materials is likely to be advantageous in most cases, because potassium salts are much more valuable (as by-products) than sodium salts.
4. The tests demonstrate the feasibility of alkali separation in a relatively short time-period, using the type of reactor described in the previous quarterly report.

Further tests of this type will be carried out, using different initial sulfate-phase compositions, especially with high potassium contents, to determine the maximum tolerable levels of potassium in the sulfate melt for any given degree of alkali removal. It is also important to determine how much of the sulfate contained in the lower layer is mechanically trapped. Clearly, it is important to minimize mechanical entrapment and maximize alkali removal.

2.4 X-Ray Diffraction Studies of Products

The upper (sulfate) layer materials from five of the fusion tests were examined by powder x-ray diffraction methods, along with three of the corresponding lower layer materials (slags). Results are given in Table 3.

It is clear from these results that the lower layer materials are basically true "glasses", because they give a broad "hump" as their x-ray pattern. They are frequently contaminated with small amounts of crystalline alkali and calcium sulfates, due to imperfect separation, which lends some credence to the suggestion that much of the sulfate in the slag layer is present in a mechanically "trapped" form.

The molten sulfate phase crystallizes on cooling to give various solid phases. Calcium langbeinite ($K_2Ca_2(SO_4)_3$) and anhydrite ($CaSO_4$) frequently coexist. When excess Na_2SO_4 is present, the main sodium-rich phase formed seems to be meta-thenardite (Na_2SO_4), with perhaps a little glauberite ($Na_2Ca(SO_4)_2$). There is also an unidentified phase which probably contains K_2SO_4 and Na_2SO_4 , and may be related to apthitalite (a mixed sodium-potassium sulfate). It would be of interest to determine the true composition of this unidentified phase.

3. Further Work

We are now nearing the end of Phase I of this study. The work has taken a somewhat different course from that envisaged in the original work program, due to the success of the sulfate fusion technique developed during the study. As a result, we will not be able to complete the designs for the bench-scale reactor required in Phase II of the study. However, as a result of negotiations between PCA and Mr. P. J. Wooding, it is fairly clear that a sulfate-fusion furnace, similar to the one described in the previous report, can be built. Mr. Wooding runs a company which specializes in designing and building high temperature metallurgical furnaces, which involve the type of technical problems which will no doubt occur in the design and construction of a sulfate-fusion reactor. There are probably few alternatives to using his company as a subcontractor in Phase II. Mr. Wooding appears to be interested in the project, and feels that it should be possible to design and build a reactor

similar to the type that I have proposed, including the system for handling the molten slag and reintroducing it into the kiln. However, due in part to time limitations, it will not be possible to obtain a detailed design for the bench scale reactor before the end of Phase I, in July 1980. As a result, I am proposing that the design of the reactor be made part of the Phase II proposal, to be submitted to DOE in April 1980, with hopes of commencing Phase II in October 1980. The success of the laboratory work so far augers well for the future.

As a result of this change of plan, we will carry out some more detailed laboratory studies in the remaining 6 months of Phase I, in order to improve our understanding of the sulfate fusion technique, and of the properties of the slag produced by it. A good understanding of slag properties (and their dependence on composition) will be essential if the slag is to be handled in the molten state and introduced to the cement kiln without excessive cooling. Such properties as viscosity, density, surface tension and heat capacity, and their dependence on temperature, must be studied. Some of this work may be carried out in the laboratory. Initially, however, a considerable amount of literature research must be done. This will probably take up the bulk of the work remaining in Phase I, leaving the majority of the laboratory testing to Phase II.

A further area which will be examined in some detail in the next 6 months will be the likely energy-efficiency of the sulfate-fusion method as applied to cement manufacture. We will attempt to construct theoretical energy balances for kilns

with sulfate-fusion furnaces, and compare these with existing techniques for alkali removal. Preliminary calculations have given encouraging results.

TABLE 1

Fusions with CaSO_4 and CaCl_2 or $\text{Mg}(\text{NO}_3)_2$

Run No.	Raw Material	Admixtures	Weight Ratio	Burning Conditions		Analysis of "Lower Layer"								Uncorrected Reduction in Alkali Content, Relative to Raw Material, %		
				Time, min.	Maximum Temperature, °C	Al_2O_3 %	Na_2O %	K_2O %	Uncorrected N/A	SO_3 %	Cl^- %	N/A Corrected for Alkali Sulfate and Chloride*		Na_2O	K_2O	Total Equivalent Alkali
P33	Ignited Fly Ash 29612	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	1:1:0.2	30	1300	20.0	0.23	1.71	0.0678	1.46	- (MgO = 5.4%)	0.0113		25.3	35.7	34.1
P34	Fly Ash 21469	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	1:1:0.2	30	1300	21.7	0.37	1.69	0.0683	1.15	- (MgO = 3.0%)	0.0273		15.6	28.2	25.4
P35	Antrim Shale	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$	1:1:0.1	30	1310	10.7	0.29	1.26	0.1046	0.29	1.152	-0.0105		31.7	53.6	49.4
P36	Shale A150	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$	1:1:0.1	20	1280	18.7	0.05	2.62	0.0949	1.12	0.093	0.0442		44.3	61.1	60.8
P37	Dur kee Clay	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$	1:1:0.1	30	1310	10.7	0.95	1.02	0.1515	1.92	0.028	0.0103		16.8	27.3	21.5
P38	Dur kee Clay	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$	1:1:0.1	10	1300	10.8	0.86	0.82	0.1296	1.15	0.194	0.0315		25.4	42.1	32.8
P39	Antrim Shale	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$	1:1:0.1	20	1280	11.0	0.30	1.63	0.1248	2.23	0.041	-0.0354		31.3	41.6	39.6

TABLE 1 (Continued)

Fusions with CaSO_4 and CaCl_2 or $\text{Mg}(\text{NO}_3)_2$

Run No.	Raw Material	Admixtures	Weight Ratio	Burning Conditions		Analysis of "Lower Layer"							Uncorrected Reduction in Alkali Content, Relative to Raw Material, %		
				Time, min.	Maximum Temperature, °C	Al_2O_3 %	Na_2O %	K_2O %	Uncorrected N/A	SO_3 %	Cl^- %	N/A Corrected for Alkali Sulfate and Chloride*	Na_2O	K_2O	Total Equivalent Alkali
P40	Clay PDD 103	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$	1:1:0.1	20	1280	13.6	0.30	0.98	0.0695	4.65	0.194	-0.2077	38.9	50.4	47.2
P41	Clay PDD 118	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$	1:1:0.1	20	1280	16.0	0.12	2.00	0.0898	1.69	0.329	-0.0099	42.7	56.9	55.9
P42	Fly Ash 21469	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$	1:1:0.1	30	1310	21.3	0.30	0.64	0.0339	1.38	0.805	-0.0493	30.3	72.3	63.0
P43	Shale PDD 108	$\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, $\text{CaCl}_2 \cdot 6\text{H}_2\text{O}$	1:1:0.1	20	1280	4.8**	0.25	0.72	0.1508	16.84**	2.896	**	12.8	30.2	25.0

Notes: *Calculated on the assumption that SO_3 and Cl^- are entirely in the form of alkali salts which are mechanically "trapped" in the lower layer.

A negative value indicates that excess SO_3 is in lower layer, presumably as CaSO_4 .

**These results indicate poor melt separation.

TABLE 2

Results of "Powder Drop" Fusion Tests

Run No.	Raw Material	Weight Ratio ¹ Raw Material/ Sulfate Melt	Composition of "Lower Layer"							Change in Alkali Content Relative to Raw Material, %		
			Al ₂ O ₃ %	Na ₂ O %	K ₂ O %	Uncor- rected N/A	SO ₃ %	Corrected ³ Na ₂ O, %	Corrected ³ N/A	Na ₂ O, Corrected for SO ₃ ³	Uncorrected K ₂ O	Total Equivalent Alkali, Corrected for SO ₃ ³
P44	Illite	0.46	16.3	3.06	0.34	0.2015	2.33	1.26	0.0908	+114.7	-90.8	-50.9
P45	Microcline ²	0.42	0.26 ²	9.44	5.40	-	-	-	-	-	-	-
P46	Illite	0.54	16.5	3.13	0.56	0.2120	1.27	2.15	0.1524	+262.0	-85.0	-17.6
P47	Albite	0.38	20.3	5.88	0.40	0.3026	3.72	3.00	0.1607	-68.4	-72.6	-68.7
P48	Montmorillonite	0.40	17.5	4.35	0.23	0.2572	1.12	3.48	0.2077	+84.1	-57.6	+62.3
P49	Antrim Shale	0.38	10.6	2.15	0.44	0.2301	3.57	-0.61 ⁴	-0.0306 ⁴	-245.0 ⁴	-83.6	-114.8 ⁴
P50	Shale A150	0.46	18.9	2.23	1.20	0.1598	1.43	1.12	0.1012	+1135	-82.4	-58.2
P51	Clay PDD 118	0.39	17.1	3.49	0.77	0.2337	3.57	0.73	0.0721	+225.9	-84.5	-64.6

Notes: 1) A mixture of four parts CaSO₄:one part Na₂SO₄ was used in all cases. Furnace temperatures were 1300°C in all cases.

2) This was clearly the sulfate layer and not the slag layer. They were difficult to distinguish in this case.

3) Corrected on the assumption that all SO₃ in the lower layer is trapped as Na₂SO₄ and may be regarded as "extractable."

4) These values indicate excess sulfate in the slag layer, presumably as CaSO₄.

TABLE 3

X-Ray Diffraction Analyses

Sample	Compounds Detected and Comments
<u>P11T:</u> Upper layer from Microcline/CaSO ₄ fusion	Mainly anhydrite (CaSO ₄), with a considerable amount of calcium langbeinite (K ₂ Ca ₂ (SO ₄) ₃). Possible traces of Na ₂ SO ₄ and FeSO ₄ .
<u>P17T:</u> Upper layer from Muscovite/CaSO ₄ fusion	Mainly calcium langbeinite, with a lesser amount of anhydrite. Possible traces of Na ₂ SO ₄ and FeSO ₄ .
<u>P46T:</u> Upper layer from Illite/CaSO ₄ / Na ₂ SO ₄ fusion	Mainly anhydrite, with lesser amounts of metathenardite (Na ₂ SO ₄ (I)). Possible traces of calcium sulfoaluminate (4CaO·3Al ₂ O ₃ ·SO ₃) and glauberite (Na ₂ SO ₄ ·CaSO ₄). Also, an unidentified compound with a strong peak at about 30.6° 2θ (2.92 Å), probably a mixed sodium/potassium sulfate.
<u>P47T:</u> Upper layer from Albite/CaSO ₄ / Na ₂ SO ₄ fusion	Similar to P46T, but without the unidentified compound, presumably because of the low potassium content in albite.
<u>P51T:</u> Upper layer from Clay PDD 118/ CaSO ₄ /Na ₂ SO ₄ fusion	Intermediate between XRD patterns of P46T and P47T, presumably because of the intermediate potassium content
<u>P46L:</u> Lower layer from Illite/CaSO ₄ / Na ₂ SO ₄ fusion	Mainly glass - a broad "hump" from 17 to 37° 2θ, peaking at about 29°, with small sub-peak at 35.4°. A separate, slightly broadened peak occurred at 48.8°.
<u>P47L:</u> Lower layer from Albite/CaSO ₄ / Na ₂ SO ₄ fusion	Mainly glass - very similar to P46L, but broad "hump" shifted by about 1-2° to lower angles. Peak at 48.8° was also present. Some sharp peaks due to anhydrite were superimposed on the broad "hump".
<u>P51L:</u> Lower layer from Clay PDD 118/ CaSO ₄ /Na ₂ SO ₄ fusion	Intermediate between P46L and P47L, except for strong peak at 31.2° 2θ, which may be due to Na ₂ SO ₄ .