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
August - October 1979

Submitted by

Ellis M. Gartner

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

December 1979

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED
RB

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
August-October 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
Principal Investigator

1. Summary

Further work on the "chloride volatilization" technique for removal of alkalies from argillaceous materials was carried out. Although this method shows some promise, it presents considerable technical problems and no significant reductions have been made in the length of time required to remove the alkalies in this way.

Fortunately, the results of tests using calcium sulfate to decompose the raw materials have been very encouraging. Based on these results, a whole new concept of the alkali separation technique has been developed. The new method involves a high-temperature liquid phase separation to remove the alkalies in the form of a mixed alkali/calcium sulfate melt. This obviates the need to waste large amounts of hot gases through a bypass. A low alkali "slag" is produced in the sulfate fusion, and is separated from the sulfate melt by gravity. The slag can then be directed into the cement kiln in some manner, the exact nature of which will require further research.

Encouraging results have been obtained in laboratory tests in which CaSO_4 has been fused with 13 different high-alkali

minerals, some of which are typical cement plant raw materials. Calculations made on the existing data suggest that this process should allow the production of low-alkali cements from high-alkali raw materials with an overall energy requirement of as low as 3.0 MBtu per ton of clinker, and with no need to discard any waste kiln dust.

2. Alkali Volatilization Using Calcium Chloride

Experiments were continued using mixtures of calcium chloride and calcium carbonate to vaporize alkalies from the minerals at high temperatures in a tube furnace.

Previous results had been obtained using samples of about 2-4 grams of the mineral plus additives in small alumina boats (2 cm wide x 1 cm deep x 10 cm long). In order to test for the kinetic effects of diffusion through the bed of material, one of the test series (using ultrafine "pure" minerals) was repeated using samples of only 0.6-0.75 grams, about one fifth of the "normal" sample size. Since the free surface area exposed to the gas stream was only slightly decreased (due to some tapering of the boats), these weights represent an increase of about a factor of 4 in free surface: mass ratio for the samples, or approximately a factor of 4 in the thickness of the sample layer. Burns were carried out in an atmosphere of 2 litres/minute of flowing N_2 at $1000^\circ C$ for 30 minutes. Results are shown in Table 1.

It is clear that there was a slight increase in alkali volatilization in the "extra-thin-layer" samples, especially

with the two feldspars (albite and microcline). The only sample which showed the reverse trend was illite; however, this can be explained on the assumption that oxidation of sulfur to give alkali sulfate opposes alkali volatilization and is more rapid for the thin layer, in this case.

The improvements in alkali volatility are not very great for the muscovite, montmorillonite (and of course the illite), which are more typical of cement plant minerals. Thus, although these results do suggest that diffusion plays an important role in alkali vaporization, they do not suggest that it is the major limitation on the reaction rate under these conditions.

Vaporization tests were also carried out on the last four of the "typical" cement plant minerals, using CaCO_3 and $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ as admixtures. Results are given in Table 2. These runs were carried out in a nitrogen atmosphere, as opposed to the air atmosphere used previously (see Table 6 of the quarterly report for February-April 1979). A new and simpler method was used to estimate the degree of alkali volatilization. All products were analyzed for SiO_2 as well as alkalis. Since SiO_2 does not vaporize appreciably during the experiment, the ratio of alkalis: SiO_2 is an excellent indication of changes in alkali content. The values for the original minerals are given in Table 3 and since the admixtures contain no SiO_2 , they do not affect the ratio.

Also used for comparison is the ratio of total alkali (expressed as equivalent Na_2O) to the total alumina (Al_2O_3). This ratio, designated N/A, is most useful for comparing the

alkali level in the various treated and untreated raw materials. The reason for this is that most high-alkali clays and shales are desirable mainly for their Al_2O_3 content, other elements being secondary. Since the Al_2O_3 content of most common portland cements does not exceed 7% (and is usually about 5-6%), then an N/A ratio of less than 0.0857 will ensure a "low-alkali" cement, i.e., less than 0.6% alkali as Na_2O , providing that no alkali comes from the other minerals in the raw mix.

The results shown in Table 2 are relatively good compared to earlier results obtained with the other minerals. Quite large reductions in alkali content were obtained by exposure to a flowing N_2 atmosphere for 30 minutes at 1000°C , and the N/A ratio of the products were almost all low enough to give low-alkali cements.

3. Other Methods of Alkali Removal

Two new methods were devised and tested. These are discussed below.

3.1 Amides

Since the amides of sodium and potassium both vaporize at very low temperatures (about 400°C), an attempt was made to vaporize the alkalies as such. Albite was dried at 230°C to ensure the complete absence of free water, which is known to decompose amides as shown below:

A mixture of approximately equal parts of calcium nitride (Ca_3N_2) and the ground, dried albite was placed in the tube furnace at temperatures between 500 - 700°C and times up to

1 hour, in a current of dry ammonia gas. It was hoped to vaporize the alkalies by a reaction such as:

The products were analyzed for SiO_2 and alkalies, and the results are given in Table 4. It is clear that only a very slight reduction in the alkali content of the samples occurred. The greatest reduction in Na_2O content (4%) occurred at the lowest temperature (500°C , 60 minutes). This did not appear to be a promising method of alkali removal, so no further tests were carried out.

3.1 Sulfate Fusions

Work by Glasser* has shown that the sulfate phases in portland cement clinker form a liquid phase which is immiscible with the normal clinker liquid phase, and floats on top of it. It was decided to try to use this as a means of separating alkalies from the alkali rich minerals, since it might well be possible to "tap off" the molten sulfate layer from the molten alumino-silicate "slag" layer and only add the "slag" to the cement kiln. It was decided to attempt this by igniting mixtures of the minerals with calcium sulfate at high temperatures in covered platinum concibles.

Initial results were very encouraging. In the first test, 4.00 grams of a finely ground mixture of 2 parts of microcline (ideal formula KAlSi_3O_8) with 1 part calcite (CaCO_3) and 1 part gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) were placed in a small covered platinum

*Note: F.P. Glasser, personal communication

crucible and heated at 1300°C for approximately 70 minutes in an electric muffle furnace, in an air atmosphere. The crucible was quenched rapidly in a water bath. When the contents were examined, two layers were found: a pale green upper layer and a pale brown glassy lower layer. The two layers could be separated easily by scraping. It appeared that they must have been immiscible liquids at 1300°C . When separated and weighed, there were about 0.370 grams of the upper layer and 2.856 of the lower layer. Partial chemical analyses of the two layers gave the following results:

	<u>K₂O</u>	<u>Na₂O</u>	<u>CaO</u>	<u>SO₃</u> (by Leco)
Upper layer	21.3%	3.8%	20.6%	56+4%
Lower layer	5.2%	1.1%	28.0%	5.94%

It is clear that the upper layer consists largely of a mixture of calcium and alkali sulfates, whereas the lower layer is essentially an aluminosilicate glass in which the excess CaO has dissolved. Some of the alkali has been removed from the lower layer. The lower layer also has dissolved some sulfate, but in fact the molar SO_3 content of this layer is almost exactly equal to the molar alkali content. This suggests that the glassy aluminosilicate layer contains the remainder of its alkali in the form of sulfates which were either "trapped" in the liquid in tiny droplets at high temperatures, or else were dissolved in it.

The results of this experiment suggested that sulfate fusions, using CaSO_4 as the sulfate source, have considerable potential as a means of separating alkalis from feldspars and other alkali-rich minerals. If the two melts could be separated

at a high temperature, the alkali/calcium sulfate melt could be tapped off and solidified to give a useful by-product, rich in potash and sulfur, with applications as a fertilizer, etc. The aluminosilicate "slag," with a low alkali content, could be added to the other raw materials (CaCO_3 , Fe_2O_3 , etc.) in the correct proportions, in the cement kiln, while still molten. This would result in a method of low-alkali cement production with minimal heat losses, and the production of a valuable by-product.

In order to test this method on the other raw materials, further tests were carried out. These are discussed in the following section.

4. Further Sulfate-Fusion Tests

Sulfate-fusion tests were carried out on five "pure" minerals and eight "typical" minerals. The minerals were those used previously, and their partial analyses are shown in Table 3. Mixtures of minerals with CaSO_4 and Fe_2O_3 , in various proportions, were fused at temperatures from 1250°C - 1360°C . In most cases, two layers were formed, the upper layer containing alkali and calcium sulfates, and the lower layer being a low alkali aluminosilicate slag. In many cases the sulfate layers were in little "pockets" near the surface of the slag, and were not easily separated by scraping. In these cases, in order to obtain sufficient slag for analysis, it was necessary to break up the slag into small pieces (about 1 mm or longer) and wash these pieces in distilled water to remove the sulfates.

Two tests (P4 and P6) were carried out in which the slags were analyzed fully for the major oxides. These tests showed that, within experimental error, all the SiO_2 , Al_2O_3 and Fe_2O_3 contained in the original minerals ended up in the slag. Therefore, it was decided that analyses of the slags for alkalis and silica were sufficient to determine the degree of alkali removal. The total alkali to alumina ratio, N/A, could also be determined from these results and used to assess the alkali content of the products, as discussed in section 2.

Twenty-three tests have been carried out to date. The results of these tests are given in Table 5. Calculated analyses of the sample before and after the test are given in Table 6. In calculating the figures in Table 6, the following assumptions were made:

- a. All of the SiO_2 , Al_2O_3 , Fe_2O_3 , MgO , and TiO_2 contained in the original mix remained in the slag layer.
- b. All of the sulfur (as SO_3), and all of the alkali not found by analysis in the slag, were contained either in the alkali/calcium sulfate melt or lost to the atmosphere as vapors.
- c. The balance of the slag composition not accounted for by Na_2O , K_2O , SiO_2 , Al_2O_3 , Fe_2O_3 , MgO and TiO_2 consisted of CaO . The rest of the CaO was in the sulfate melt.
- d. The L.O.I's of the minerals (obtained at 950°C in air), as used in this study, did not include any loss

of SO_3 or alkalies, and were unaltered by intermixing of the minerals with $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ or Fe_2O_3 .

None of these assumptions are completely accurate, but are sufficiently so for a reasonable set of comparative results to be obtained, as shown in Table 6. In fact, it is clear from the analyses as P4 and P6 that some SO_3 (typically 1-2%) is retained in the slag. The CaO content of the slag will generally be slightly lower than calculated on the basis of assumption (c). This probably accounts for the negative calculated CaO content in the sulfate melt in a few cases.

It is not possible to make an accurate estimate of alkali loss by vaporization. However, most of the indications are that the major weight losses were due to vaporization of SO_3 , which probably decomposes to $\text{SO}_2 + 1/2 \text{O}_2$ on vaporization at these temperatures. It is well-known that reducing conditions result in breakdown of alkali and calcium sulfates to give the oxides plus SO_2 gas, and there was evidence, in some of these tests, that this occurred during the run, especially in the case of fly ashes, which generally contain either carbon or metallic iron or reduced iron compounds such as FeS or FeO. In the case of fly ash 29612 (mineral #7), no separation of sulfate layers occurred during the test run because of reduction. In a later test, the fly ash was oxidized in air before the sulfate fusion, and gave improved results.

The results in Table 5 show that, in several cases, low N/A ratio slags were obtained, which would have been suitable for making low alkali cements. Especially encouraging were the

results obtained with muscovite and illite, which are generally difficult minerals to handle in a cement kiln. Temperatures in the range 1300-1350°C appear to be necessary to obtain good melt formation and separation. However, the duration of the tests seemed to have little effect on the degree of alkali removal, at least in the 10-30 minute range. Most of these experiments were carried out at 1300°C initially and reheating to a higher temperature was used if no separation had occurred at that temperature. Once separation had occurred, it appears that further time at that temperature results in very little change in alkali content. This suggests that, once the slag melt viscosity is low enough for the sulfates to float to the surface, further reaction is slow because it can only occur at the interface between the two liquids. A small amount of sulfur remains in the slags, probably by mechanical entrapment as alkali sulfate, but possibly in solution. Sulfide sulfur is fairly soluble in most metallurgical slags, and some may be present in these slags; however, it is likely that S^{2-} would be unstable in an air atmosphere and in the presence of excess SO_4^{2-} .

The calculated slag compositions shown in Table 6 are of use in determining the likely properties of these slags. It was found that additions of Fe_2O_3 resulted in apparent decreases in slag viscosity in some cases. However, the amounts of Fe_2O_3 added were somewhat excessive, since most portland cements should have an Al_2O_3/Fe_2O_3 ratio of about 1.5 - 2.0. Fairly good results were achieved in low-iron systems, e.g., runs Pl2, Pl3 and P29.

Future work in this project will be aimed at answering the following questions:

- a. What is the optimum composition of the slag melt to give minimum viscosity at the lowest possible temperature, and yet be suitable for use as part of the cement raw mix?
- b. What are the major kinetic factors determining the rate of alkali removal by the sulfate fusion method, and how can a knowledge of these factors be applied to improve the process?
- c. What are the effects of "impurities" such as MgO , TiO_2 , P_2O_5 , F^- , Cl^- , etc. on this process?
- d. Is there a limit to the amount of alkali which can be removed by sulfate fusion?
- e. Is there a limit to the alkali content of the sulfate-rich layer which is discarded? (Clearly, a high K_2SO_4 content would be desirable if the material is to be used as a potash source.)

The answers to these questions will have a considerable influence on the detailed design of the reactor in which the sulfate fusion will take place. A basic design has been drawn up, however, with a view to later modification if necessary. This design is presented in the following section.

5. Proposed System for Alkali Removal by Sulfate Fusion

5.1 Design for Sulfate-Fusion Reactor

The sulfate-fusion method for removing alkalies from feldspars, micas, shales, clays, etc., requires that the resulting low-alkali aluminosilicate slag be kept hot enough for pouring while within the reaction vessel. The main heat loss route will presumably be through the walls (conduction). A serious problem will also be attack of the slag on the refractory lining. The method of heating the slag also raises problems. Arc heating and induction heating are not very feasible, since the glass will have rather low conductivity relative to the sulfate melt. Carbon electrodes would tend to reduce the sulfate melt, which is undesirable.

A solution to these problems is presented here. If the aluminosilicate "slag" layer were floating on a molten (or solid) metal, then the floor of the furnace would be protected from the corrosive effects of the slag. Moreover, the metal floor could readily be heated electrically, preferably by induction. This would provide a means of balancing thermal losses from the furnace, and allow restart in the event of a shutdown.

A schematic diagram of the proposed furnace is given in Figure 1. The incoming feed, i.e., alkali-rich mineral plus CaCO_3 (or CaO or CaSO_4), is preheated in a cyclone tower, which also serves to recapture SO_2 , SO_3 and alkali vapors, and to reduce heat losses. It falls slowly through the alkali/calcium sulfate melt and, as it does so, most of the alkalies are removed. The residue forms an alumino-silicate slag which is

also rich in calcium oxide. The exact composition of this slag may be varied by altering the CaO , Fe_2O_3 and MgO content of the feed by adding these components; SiO_2 could also be added if necessary, as well as CaF_2 and CaCl_2). The slag is heated from above by transfer of heat through the sulfate melt, which in turn is heated by a gas or coal burner above the surface. Care must be taken to keep the surface atmosphere sufficiently oxidizing so that there is not excessive decomposition or vaporization of the sulfate melt. The metal base (probably either molten iron or molten copper) is heated electrically, preferably by induction, and transfers heat to the slag melt by convection. The heavy refractory walls are well insulated to reduce heat losses, but in the slag zone sufficient heat loss by conduction must be permitted in order to reduce the erosion to a minimum, i.e., by building a protective solid or semi-solid slag layer on the surface. The slag tapping tube will clearly have to be made from a special alloy or refractory; it may need to be water-cooled. The slag can probably be kept oxygen-free at this point, which should be advantageous.

The molten metal, (probably iron or copper), will tend to oxidize rapidly in the presence of air, but its rate of oxidation in this case will be greatly reduced by the presence of a thick slag layer through which oxygen cannot diffuse rapidly. However, it is to be expected that the slag layer would be reduced by iron to give an FeO -rich layer of slag near the bottom. It is hoped that vertical diffusion through the slag melt would be slow enough such that an "oxidation gradient" may

be maintained in it, with the FeO - and sulfide-rich layer at the bottom, and an Fe_2O_3 -rich layer at the top. Slag tapping should probably be from near the top, as ferric iron is preferable in the cement kiln. If excessive sulfide levels occur in the metal, a blast of air through the base should serve to reoxidize FeS to $\text{FeO} + \text{SO}_2$, and should help reduce the sulfide content of the slag. If depletion of iron becomes a problem, further additions of iron could be made in the form of iron scrap or iron sulfides (FeS_2 , etc.). Slow dissolution of iron in the slag would probably be acceptable as long as the $\text{Fe}_2\text{O}_3:\text{Al}_2\text{O}_3$ ratio of the slag were kept sufficiently low for manufacture of the desired type of portland cement.

If molten copper were to be used, the problem of oxidation would be greatly reduced, since copper is much less electropositive than iron. Nevertheless, a small amount of Cu_2O might dissolve in the slag. This might not be harmful, providing that the cost of the lost copper were not prohibitive.

5.2 The Kiln System

If a sulfate-fusion reactor is added to a preheater kiln, (with or without a precalciner), various modifications will be required. Some of the possible options are outlined here, as a basis for future development.

In order to achieve the maximum degree of alkali removal with minimum heat losses, the sulfate-fusion reactor should be set up so that the molten, low-alkali "slag" can be fed directly into the cement kiln system at a suitable point, probably close to the back end of the kiln. It will be necessary to design a

system in which the molten slag is intimately mixed with the other low-alkali calcareous raw materials (already partially calcined CaCO_3 with some SiO_2 , Al_2O_3 and Fe_2O_3 , etc.). The hot calcareous feed generally enters the kiln via a feed chute from the bottom of the 4th stage cyclone in the preheater string. Addition of the slag could be via a "spinning wheel" distributor (as used in rockwool manufacture), which would throw off many thin filaments or fine droplets of slag into the bed of hot calcareous feed.* Other systems might be devised. The composition of the slag will probably be slightly acidic, i.e., rich in SiO_2 and Al_2O_3 relative to CaO and MgO . The reaction between an acidic slag and calcined lime is likely to be strongly exothermic. Therefore, if the feed entering the kiln consists of slag plus almost fully calcined limestone, a rapid rise in temperature should occur in the kiln. This would be beneficial to kiln operation, because the length of the kiln could probably be reduced considerably for a given production rate. It should also make it possible to burn less fuel at the kiln burner, and could result in a reduction in kiln shell heat losses.

Another modification which would be beneficial to the system as a whole would be the use of kiln exit gases to preheat the raw materials which enter the sulfate-fusion reactor. If all, or at least a considerable portion of the kiln exit gases are diverted into the "alkali-separator" chamber and preheater, then the effects should be beneficial for several reasons:

*Note: N. R. Greening, Personal Communication.

- a. Any alkali sulfates or chloride, etc., vaporized in the kiln itself will recondense on the incoming alkali-rich feed, and will ultimately be removed from the cycle in the alkali sulfate melt. This will improve the degree of overall alkali removal above that indicated by single fusion tests in an open system, i.e., as in the laboratory tests.
- b. Sulfur oxides (mainly SO_2) from the kiln fuel could be used as the sole source of sulfur in the system. SO_2 will react rapidly with CaCO_3 or CaO at temperatures in the range $800\text{--}1000^\circ\text{C}$, (in the presence of a few percent O_2), to give CaSO_4 . Therefore, SO_2 in the kiln exit gases will react with CaCO_3 in the incoming feed, (mixed with the argillaceous feed component), to give CaSO_4 which will react in the sulfate-fusion reactor. This will serve two purposes. It will make the use of high-sulfur fuels beneficial to the manufacturing process, and it will also improve the overall thermal efficiency of the process, since waste heat from the kiln will be used to preheat the incoming raw materials. Moreover, if a very short rotary kiln is used, then kiln exit gases will be hotter than is the case in existing precalciner systems, and may require only a small amount of excess fuel to be burned in the sulfate-fusion reactor.

c. Passage of kiln exit gases through the "alkali-separator" preheater string will also help to remove alkalies, sulfur and chlorides that may have come from the limestone or other raw materials entering the kiln with the calcareous feed. The system is, in one sense, a kind of extreme case of a precalciner kiln operating with a large degree of bypass. However, it has the advantage that no hot, dusty bypass gases need to leave the system. Instead, alkalies, sulfur, and chloride will leave the system in the alkali-sulfate melt; (it is known that alkali chlorides are soluble in such melts). The heat losses will only be those due to the sensible heat of the alkali-sulfate melt. The kiln exit gases will be used effectively to pre-heat incoming feed, and most of their available heat can be used in this way, before they leave the system at temperatures as low as 300-350°C from the top of the preheater strings on both the argillaceous feed and calcareous feed preheaters. "Kiln dust" collected from the preheater towers can probably all be returned to one or both preheaters. Therefore, no dust need be wasted from this system. Of course, separate grinding facilities will be required for the two types of kiln feed (argillaceous and calcareous).

There are many possible variations on this method. For example, it may be impossible to add the slag directly to the kiln as a melt. In such a case, the slag would have to be

quenched (possibly granulated with water) and reground before mixing with the kiln feed in the main preheater string. The kiln system would be similar, and kiln exit gases could still be used to preheat the argillaceous feed. This method is likely to consume more energy than the direct slag feed to the kiln method, because of the loss of the sensible heat in the slag. Nevertheless, this would only be of the order of 0.3-0.5 MBtu/ton, depending on slag composition, etc. Perhaps a more serious consideration would be in the extra grinding energy required to regrind the slag.

In order to attempt to quantify the possible energy savings possible by using the sulfate-fusion method, some rough comparative calculations have been made. They indicate that the sulfate-fusion method could result in production of low-alkali cements at energy requirements of about 3.0 MBtu/ton or less, which is better than that achievable with existing precalciner systems when high-alkali raw materials are used. Further, more detailed calculations will be carried out and discussed in the next quarterly report.

Fig. 1: Sulfate-Fusion Reactor
Preliminary Design Sketch

CR 7574-4330
November 1979

FIGURE 1: Sulfate-Fusion Reactor, Preliminary Design Sketch

Key

- A: Preheated-feed inlet
- B: Gases to feed preheater
- C: Fuel and air, to burner
- D: Sulfate melt tapping port
- E: Slag tapping port
- F: Molten metal tapping or filling port
- G: Air-blast inlet, if required
- H: Induction-heating coils
- I: Preheated feed falling through flame and into melt
- J: Hot gases to preheat cyclones
- K: Sulfate-melt layer
- L: Slag layer
- M: Molten metal
- N: Dense refractory lining
- O: Lightweight Refractory casing
- P: Bottom preheater cyclone

TABLE 1

Extra-Thin-Layer Chloride Vaporization Tests

Mineral*	"Extra-Thin-Layer" Burns				"Normal" Burns**			
	Weight of Sample, grams	Observed L.O.I. %	Alkali in Product		Weight of Sample, grams	Observed L.O.I. %	Alkali in Product	
			%Na ₂ O	%K ₂ O			%Na ₂ O	%K ₂ O
Albite	0.6881	25.20	4.30	0.18	4.0408	19.29	5.80	0.66
Muscovite	0.7229	22.26	0.33	4.60	3.5176	22.25	0.31	4.10
Montmorillonite	0.7262	21.69	1.80	0.53	3.5075	21.33	1.85	0.48
Microcline	0.5933	21.37	1.00	6.50	3.3739	18.05	1.46	8.34
Illite	0.6009	23.30	0.41	1.90	3.0455	25.93	0.36	1.48

Notes: *All sample mixes consist of mineral, with CaCO₃ and CaCl₂·2H₂O added in the proportions used in the previous tests (see Table 4 of the Quarterly Report for May-July 1979). All of the minerals were ground to -325 mesh. Burns were carried out at 1000°C in N₂ (at a flowrate of about 2 l/min.), for 30 minutes. The same size alumina boats were used for all burns; only the sample sizes differed.

**Results from Table 4 of the Quarterly Report for May-July 1979.

TABLE 2

Chloride Vaporization Burns on Four "Typical" Minerals

Mineral	Admixtures, Expressed as Parts per 100 Parts of the Mineral		Analysis of Product, After Burning for 30 min. in N ₂ at 1000°C				N/A* for Pure % Alkali Unburned Vaporized Mineral	
	CaCO ₃	CaCl ₂ •2H ₂ O	SiO ₂	Na ₂ O	K ₂ O	N/A*		
Clay PDD 103 #5	20	5.2	53.6	0.51	1.60	0.0904	0.1316	31.3
Shale PDD 108 #6	20	3.2	35.6	0.30	0.48	0.0816	0.2011	59.4
Fly Ash 29612 #7	20	6.0	49.3	0.28	2.15	0.0754	0.1029	26.7
Clay PDD 118 #8	20	8.6	54.6	0.16	2.10	0.0873	0.2038	57.2

*Note: N/A = ratio of total alkali expressed as Na₂O over total aluminum as Al₂O₃

TABLE 3

Analyses of Raw Materials: Summary

Mineral	Sample Code No.	$\frac{\text{Na}_2\text{O}}{\text{SiO}_2}$	$\frac{\text{K}_2\text{O}}{\text{SiO}_2}$	$\frac{\text{SiO}_2}{\text{Al}_2\text{O}_3}$	$\frac{\text{Fe}}{\text{Al}_2\text{O}_3}$	N/A
<u>"Pure" Minerals</u>						
Kaolin	PDC 155	0.0013	0.0029	1.157	38.90	0.0037
Albite	PDC 156	0.1919	0.0296	2.435	23.70	0.5146
Muscovite	PDC 157	0.0147	0.2176	1.506	31.00	0.2378
Montmorillonite	PDC 158	0.0343	0.0100	3.140	17.90	0.1284
Microcline	PDC 168	0.0327	0.1793	3.782	17.40	0.5698
Illite	PDC 169	0.0124	0.0777	2.910	17.70	0.1849
<u>"Typical" Minerals</u>						
Antrim Shale	#1	0.0101	0.0642	3.949	13.84	0.2066
Shale A150	#2	0.0018	0.1335	2.700	22.75	0.2420
Durkee Clay	#3	0.0233	0.0286	4.578	13.50	0.1930
Fly Ash 21469	#4	0.0109	0.0585	1.854	28.70	0.0915
Clay PDD 103	#5	0.0117	0.0468	3.102	16.60	0.1316
M. M. Shale	#6	0.0127	0.0456	4.716	6.70	0.2011
Fly Ash 29612	#7	0.0070	0.0970	2.192	24.00	0.1029
Clay PDD 118	#8	0.0042	0.0938	3.091	17.60	0.2038

TABLE 4

Vaporization in an Ammonia Atmosphere

Sample	Time, minutes	Tempera- ture °C	Analysis of Product			
			Na ₂ O/SiO ₂ *	%SiO ₂	%Na ₂ O	%K ₂ O
Albite + Ca ₃ N ₂	60	500	0.184	45.7	8.4	1.32
Albite + Ca ₃ N ₂	30	600	0.190	45.7	8.7	1.31
Albite + Ca ₃ N ₂	30	700	0.191	45.1	8.6	1.32

*Note: The ratio of Na₂O/SiO₂ in the albite used was 0.192.

TABLE 5

Analyses of "Glassy" Alumino-Silicate Layers from CaSO_4 Fusions

Raw Material	Run No.	Admixtures, Relative to 100 parts of Raw Material	Maximum Temperature and Time	Raw Material Composition Ratios			Product "Glass" Composition Ratios		
				N/A*	$\frac{\text{Na}_2\text{O}}{\text{SiO}_2}$	$\frac{\text{K}_2\text{O}}{\text{SiO}_2}$	N/A*	$\frac{\text{Na}_2\text{O}}{\text{SiO}_2}$	$\frac{\text{K}_2\text{O}}{\text{SiO}_2}$
Albite	P4	100 parts $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	1360°C, 30 min.	0.5146	0.1919	0.0296	0.2498	0.0938	0.0139
	P10	100 parts CaSO_4 , + 22 parts Fe_2O_3	1300°C, 30 min.	0.5146	0.1919	0.0296	0.1695	0.0642	0.0083
	P16	133 parts $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ + 33 parts Fe_2O_3	1300°C, 30 min.	0.5146	0.1919	0.0296	0.1798	0.0682	0.0086
	P18	133 parts $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ + 33 parts Fe_2O_3	1290°C, 15 min.	0.5146	0.1919	0.0296	0.1616	0.0615	0.0074
Microcline	P6	100 parts $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	1360°C, 30 min.	0.5698	0.0327	0.1793	0.3417	0.0188	0.1065
	P11	100 parts CaSO_4 , + 22 parts Fe_2O_3	1300°C, 15 min.	0.5698	0.0327	0.1793	0.2567	0.0140	0.0819
	P19	133 parts $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ + 33 parts Fe_2O_3	1290°C, 15 min.	0.5698	0.0327	0.1793	0.2920	0.0157	0.0935

*Note: N/A = ratio of total alkali expressed as Na_2O over total aluminum as Al_2O_3 .

TABLE 5 (Continued)

Analyses of "Glassy" Alumino Silicate Layers from CaSO_4 Fusions

Raw Material	Run No.	Admixtures, Relative to 100 parts of Raw Material	Maximum Temperature and Time	Raw Material Composition Ratios			Product "Glass" Composition Ratios		
				N/A*	$\frac{\text{Na}_2\text{O}}{\text{SiO}_2}$	$\frac{\text{K}_2\text{O}}{\text{SiO}_2}$	N/A*	$\frac{\text{Na}_2\text{O}}{\text{SiO}_2}$	$\frac{\text{K}_2\text{O}}{\text{SiO}_2}$
Microcline	P22	As for P19, but without lid on crucible**	1300°C, 30 min.	0.5698	0.0327	0.1793	0.2545	0.0140	0.0810
	P23	As for P19, but with lid on crucible	1300°C, 30 min.	0.5698	0.0327	0.1793	0.2533	0.0138	0.0809
Muscovite	P12	100 parts CaSO_4	1350°C, 35 min.	0.2378	0.0147	0.2176	0.1037	0.0073	0.0936
	P14	100 parts CaSO_4 , + 22 parts Fe_2O_3	1300°C, 30 min.	0.2378	0.0147	0.2176	0.0681	0.0056	0.0602
	P17	133 parts $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ + 33 parts Fe_2O_3	1350°C, 15 min.	0.2378	0.0147	0.2176	0.0672	0.0056	0.0593
Illite	P13	100 parts CaSO_4	1350°C, 10 min.	0.1849	0.0124	0.0777	0.0733	0.0044	0.0316
	P15	100 parts CaSO_4 + 22 parts Fe_2O_3	1300°C, 30 min.	0.1849	0.0124	0.0777	0.0849	0.0051	0.0366
	P21	133 parts $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ + 33 parts Fe_2O_3	1300°C, 30 min.	0.1849	0.0124	0.0777	0.0903	0.0057	0.0385

*Note: All other runs were carried out with lid on crucible.

TABLE 5 (Continued)

Analyses of "Glassy" Alumino Silicate Layers from CaSO_4 Fusions

Raw Material	Run No.	Admixtures, Relative to 100 parts of Raw Material	Maximum Temperature and Time	Raw Material Composition Ratios			Product "Glass" Composition Ratios		
				N/A*	$\frac{\text{Na}_2\text{O}}{\text{SiO}_2}$	$\frac{\text{K}_2\text{O}}{\text{SiO}_2}$	N/A*	$\frac{\text{Na}_2\text{O}}{\text{SiO}_2}$	$\frac{\text{K}_2\text{O}}{\text{SiO}_2}$
Montmorillonite	P20	133 parts $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ + 33 parts Fe_2O_3	1350°C, 15 min.	0.1284	0.0343	0.0100	0.1272	0.0337	0.0104
Antrim Shale (#1)	P24	100 parts $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	1300°C, 30 min.	0.2068	0.0101	0.0642	0.1306	0.0065	0.0404
Shale Al50 (#2)	P25	100 parts $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	1300°C, 30 min.	0.2420	0.0018	0.1335	0.1735	0.0009	0.0963
Durkee Clay (#3)	P26	100 parts $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	1300°C, 30 min.	0.1929	0.0233	0.0286	0.1608	0.0196	0.0236
Clay PDD 103 (#5)	P29	100 parts $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	1300°C, 30 min.	0.1318	0.0117	0.0468	0.0952	0.0085	0.0337
M. M. Shale (#6)	P30	100 parts $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	1340°C, 15 min.	0.2013	0.0127	0.0456	0.1831	0.0116	0.0414
N. W. Clay (#8)	P32	100 parts $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	1300°C, 30 min.	0.2037	0.0042	0.0938	0.1408	0.0027	0.0651

TABLE 5 (Continued)

Analyses of "Glassy" Alumino Silicate Layers from CaSO_4 Fusions

Raw Material	Run No.	Admixtures, Relative to 100 parts of Raw Material	Maximum Temperature and Time	Raw Material Composition Ratios			Product "Glass" Composition Ratios		
				N/A*	$\frac{\text{Na}_2\text{O}}{\text{SiO}_2}$	$\frac{\text{K}_2\text{O}}{\text{SiO}_2}$	N/A*	$\frac{\text{Na}_2\text{O}}{\text{SiO}_2}$	$\frac{\text{K}_2\text{O}}{\text{SiO}_2}$
Fly Ash (#4)	P28	100 parts $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$	1340°C, 15 min.	0.0915	0.0109	0.0585	0.0733	0.0093	0.0461

*Note: N/A = ratio of total alkali expressed as Na_2O over total aluminum as Al_2O_3 .

TABLE 6

Calculated Compositions of Sulfate-Fusion Mixes

Run No.	Whole Sample, Before Ignition										Total
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	Na ₂ O	K ₂ O	TiO ₂	L.O.I.*	
<u>Albite</u>											
P4	28.85	11.85	0.50	17.59	0.03	23.30	5.54	0.86	0.05	11.35	99.92
P10	25.99	10.68	10.36	19.73	0.03	26.53	4.99	0.77	0.05	0.79	99.92
P16	21.69	8.91	12.78	17.26	0.02	23.28	4.16	0.64	0.04	11.13	99.91
P18	21.69	8.91	12.78	17.26	0.02	23.28	4.16	0.64	0.04	11.13	99.91
<u>Microcline</u>											
P6	32.90	8.70	0.41	16.64	0.02	23.29	1.08	5.90	0.03	10.73	99.70
P11	29.61	7.83	10.36	18.85	0.02	26.46	0.97	5.31	0.03	0.23	99.67
P19	24.68	6.55	12.80	16.55	0.02	23.28	0.81	4.43	0.02	10.66	99.80
P22	24.68	6.55	12.80	16.55	0.02	23.28	0.81	4.43	0.02	10.66	99.80
P23	24.68	6.55	12.80	16.55	0.02	23.28	0.81	4.43	0.02	10.66	99.80

*Note: Calculated L.O.I. excluding SO₃ or alkalies.

CR-7574-4330
November 1979

TABLE 6 (Continued)

Calculated Compositions of Sulfate-Fusion Mixes

Run No.	Observed L.O.I. of Mix	Estimated L.O.I. due to Alkalies and SO ₃					Composition of Slag					Calculated Content of Sulfate Layer and Vapor, Relative to Slag					
		Relative to Mix	Relative to Slag	Analyzed			Calculated					CaO	Na ₂ O	K ₂ O	SO ₃		
				SiO ₂	Na ₂ O	K ₂ O	CaO	MgO	Fe ₂ O ₃	Al ₂ O ₃	TiO ₂						
<u>Albite</u>																	
P4	31.46	20.11	35.69	51.2	4.80	0.71	19.2* (19.41)	0.12* (0.05)	0.80* (0.89)	21.10* (21.03)	0.09	12.02	5.03	0.82	39.58** (41.35)		
P10	10.51	9.72	16.31	43.6	2.80	0.36	17.80	0.05	17.37	17.92	0.09	15.28	5.57	0.93	44.51		
P16	31.30	20.17	36.82	39.6	2.70	0.34	17.65	0.04	23.33	16.27	0.07	13.86	4.90	0.83	42.50		
P18	18.99	7.86	14.13	39.0	2.40	0.29	17.20	0.04	22.98	16.02	0.07	11.83	5.08	0.86	41.86		
<u>Microcline</u>																	
P6	30.31	19.58	34.10	57.3	1.08	6.10	18.0* (18.55)	0.06* (0.03)	0.80* (0.71)	14.90* (15.15)	0.05	10.98	0.80	4.18	40.56		
P11	9.21	8.98	15.56	51.3	0.72	4.20	12.18	0.03	17.95	13.57	0.05	20.48	0.96	5.00	45.84		
P19	16.66	6.00	11.18	46.0	0.72	4.30	12.83	0.04	23.86	12.21	0.04	18.02	0.79	3.96	43.39		
P22	19.24	8.58	15.89	45.7	0.64	3.70	14.05	0.04	23.70	12.13	0.04	16.60	0.86	4.50	43.10		
P23	17.80	7.14	13.60	47.0	0.65	3.80	11.62	0.04	24.38	12.47	0.04	19.90	0.89	4.64	44.33		

*Note: For samples P4 and P6, these are actually measured oxide contents. The numbers in brackets are the calculated values.
Total sulfur as SO₃ was also determined, the results being as follows: P4 - 1.77% SO₃; P6 - 1.16% SO₃

TABLE 6 (Continued)

Calculated Compositions of Sulfate-Fusion Mixes

Whole Sample, Before Ignition											
Run No.	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	Na ₂ O	K ₂ O	TiO ₂	L.O.I.	Total
<u>Muscovite</u>											
P12	23.35	15.50	2.56	20.75	0.51	29.41	0.34	5.08	0.20	2.67	100.37
P14	21.02	13.95	12.30	18.67	0.46	26.46	0.31	4.57	0.18	2.40	100.32
P17	17.51	11.63	14.42	16.40	0.38	23.25	0.26	3.81	0.15	12.46	100.27
<u>Illite</u>											
P13	25.75	8.85	2.56	22.85	0.98	30.69	0.32	2.00	0.40	5.90	100.30
P15	23.18	7.97	12.30	20.56	0.88	27.62	0.29	1.80	0.36	5.31	100.27
P21	19.31	6.64	14.42	17.97	0.74	24.21	0.24	1.50	0.30	14.89	100.22
<u>Montmorillonite</u>											
P20	21.08	6.71	13.94	16.81	0.60	23.46	0.72	0.21	0.11	16.39	100.03
<u>Antrim Shale</u>											
P24 (#1)	27.33	6.92	3.04	17.32	1.20	26.70	0.28	1.76	--	17.91	102.46
<u>Shale Al50</u>											
P25 (#2)	30.71	11.38	1.90	16.36	0.38	23.35	0.06	4.10	0.45	12.59	101.28
<u>Durkee Clay</u>											
P26 (#3)	30.90	6.75	2.87	17.71	0.63	23.32	0.72	0.89	0.40	15.09	99.28

TABLE 6 (Continued)

Calculated Compositions of Sulfate-Fusion Mixes

Run No.	Observed L.O.I. of Mix	Estimated L.O.I. due to Alkalies and SO ₃		Composition of Slag								Calculated Content of Sulfate Layer and Vapor, Relative to Slag			
				Analyzed			Calculated								
		Relative to Mix	Relative to Slag	SiO ₂	Na ₂ O	K ₂ O	CaO	MgO	Fe ₂ O ₃	Al ₂ O ₃	TiO ₂	CaO*	Na ₂ O	K ₂ O	SO ₃
<u>Muscovite</u>															
P12	18.05	15.38	23.51	35.7	0.26	3.34	31.70	0.78	3.91	23.70	0.31	(-)	0.26	4.43	44.97
P14	16.14	13.74	21.18	32.4	0.18	1.95	24.02	0.71	18.96	21.50	0.28	4.78	0.30	5.09	40.79
P17	26.31	13.85	23.89	30.2	0.17	1.79	22.00	0.66	24.87	20.05	0.26	6.29	0.28	4.78	40.10
<u>Illite</u>															
P13	27.35	21.45	35.57	42.7	0.19	1.35	34.51	1.66	4.25	14.68	0.66	3.38	0.34	1.97	50.89
P15	24.20	18.89	30.07	36.9	0.19	1.35	27.32	1.40	19.58	12.69	0.57	5.41	0.27	1.52	43.97
P21	28.11	13.22	21.70	31.7	0.18	1.22	29.50	1.21	23.67	10.90	0.49	(-)	0.21	1.24	39.74
<u>Montmorillonite</u>															
P20	38.28	21.89	36.03	34.7	1.17	0.36	27.67	0.99	22.95	11.05	0.18	(-)	0.02	(-)	38.62
<u>Antrim Shale</u>															
P24 (#1)	35.70	17.79	32.87	50.5	0.33	2.04	26.50	2.22	5.62	12.79	ND	5.50	0.19	1.21	49.34
<u>Shale A150</u>															
P25 (#2)	26.66	14.07	19.70	43.0	0.04	4.14	22.91	0.53	2.66	15.93	0.63	(-)	0.04	1.60	32.69
<u>Durkee Clay</u>															
P26 (#3)	35.58	20.49	33.16	50.0	0.98	1.18	28.66	1.02	4.64	10.92	0.65	(-)	0.19	0.26	37.73

*Note: A negative calculated CaO content (-) in this column indicates that the true CaO content of the slag must be lower than that calculated here (by difference).

CR-7574-4330
November 1979

TABLE 6 (Continued)

Calculated Compositions of Sulfate-Fusion Mixes

Run No.	Whole Sample, Before Ignition										Total	
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	Na ₂ O	K ₂ O	TiO ₂	L.O.I.		
<u>Clay PDD 103</u>												
P29	(#5)	25.75	8.30	3.10	18.04	1.57	23.28	0.30	1.21	0.37	17.81	99.73
<u>M. M. Shale</u>												
P30	(#6)	15.80	3.35	1.35	30.44	0.96	24.19	0.20	0.72	0.17	22.91	100.09
<u>N. W. Clay</u>												
P32	(#8)	27.20	8.80	2.66	18.10	1.34	23.75	0.12	2.55	0.45	14.93	99.90
<u>Fly Ash 21469</u>												
P28	(#4)	26.60	14.35	4.75	16.94	0.51	23.43	0.29	1.56	0.80	11.97	101.20

TABLE 6 (Continued)

Calculated Compositions of Sulfate-Fusion Mixes

Run No.	Observed L.O.I. of Mix	Estimated L.O.I. due to Alkalies and SO ₃		Composition of Slag									Calculated Content of Sulfate Layer and Vapor, Relative to Slag			
				Analyzed			Calculated									
		Relative to Mix	Relative to Slag	SiO ₂	Na ₂ O	K ₂ O	CaO	MgO	Fe ₂ O ₃	Al ₂ O ₃	TiO ₂	CaO	Na ₂ O	K ₂ O	SO ₃	
<u>Clay PDD 103</u>																
P29	(#5)	33.13	15.32	26.48	44.5	0.38	1.50	30.57	2.71	5.36	14.34	0.64	0.61	0.14	0.59	40.23
<u>M. M. Shale</u>																
P30	(#6)	32.66	9.75	14.32	23.2	0.27	0.96	44.70	1.41	1.98	4.92	0.37	(-)	0.02	0.10	35.52
<u>N. W. Clay</u>																
P32	(#8)	26.34	11.41	19.84	47.3	0.13	3.08	26.45	2.33	4.63	15.30	0.78	5.03	0.08	1.35	41.30
<u>Fly Ash 21469</u>																
P28	(#4)	32.15	20.18	30.11	39.7	0.37	1.83	25.28	0.76	7.09	21.42	1.19	(-)	0.06	0.50	34.96

CR-7574-4330
November 1979