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

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Submitted by
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Washington, D.C.

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Use of Precalciners to Remove Alkali from Raw Material
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Summary

The attached reports deal with the results of: (1) a literature survey on the general topics of alkali volatilization and heat transfer in cement manufacturing systems, (2) A survey of on-line gas analysis techniques for alkalies, sulfur and chlorine, and (3) a series of high-temperature burns of selected ground argillaceous minerals with various chloride-containing admixtures.

The final part of the literature survey (except for two translations of foreign literature which have not yet been completed) has not turned up much further information regarding the volatility of alkalies in pure minerals. However, some useful references to heat-transfer in existing precalciner systems were found. Further literature searches will be carried out as part of the experimental work; of special importance in this regard will be a survey of existing thermodynamic data dealing with alkali volatility.

The survey of on-line gas analysis techniques for alkalies, etc, has shown that no techniques have as yet been developed to

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the stage where they can be used in a cement kiln system. However, developments in this area might be expected to occur rapidly in the next few years.

The experimental work has been successful in showing that the combined addition of CaCO_3 and CaCl_2 to several of the minerals enhances alkali volatility at 1000°C relative to addition of CaCl_2 alone, although the degree of alkali loss rarely exceeds about 50%. The greatest success was achieved with the feldspars, which also performed well with additions of a $\text{MgCl}_2/\text{NH}_4\text{Cl}$ mixture. The illite and muscovite results generally were more difficult to interpret. The kaolin and montmorillonite actually showed gains in alkali content in many of the burns, probably due to a weakness in the experimental method. As a result, future experiments will, where possible, be conducted in a tube furnace, in a flowing gas stream, to avoid sample contamination. Further work will also include the use of FeCl_3 and HCl vapors in controlled atmospheres.

1. Literature Study

The literature study was continued, and the majority of the articles and patents listed in the two PCA library studies were scanned for any useful input to the project. Two German papers, which looked to be very relevant, have now been submitted for translation. The first of these ⁽¹⁾, deals with the effects of adding alkali- and alkaline-earth chlorides to the raw mix in the manufacture of white cements. The authors claim that appreciable amounts of iron are lost from the material, presumably in the form of FeCl_3 , which is highly volatile (boiling at 315°C). Apparently, more iron is lost under reducing conditions than under oxidizing conditions. A fuller report of this paper must await our receipt of the translation. The second German reference is a series of three consecutive papers by B. Vosteen ⁽²⁾ dealing with heat transfer in pre-heater systems. It appears that these papers may be of considerable use when it comes to designing a pilot-scale kiln system using the "separate argillaceous precalciner" concept.

Other papers covered in the literature survey included one by Holden ⁽³⁾ in which the overall effectiveness of adding CaCl_2 to both wet and dry kiln systems was carefully studied. Holden found that the amount of alkali vaporized was approximately proportional to the amount of CaCl_2 added, although K_2O tended to vaporize more readily; (this may have been due to the higher initial K_2O level in the raw mix). However, the total "efficiency" of vaporization was only about 32% in the wet kiln and 48% in the dry kiln. While these "efficiency"

values are only applicable to their own particular kiln system, this paper was of interest in that it was a carefully conducted, quantitative study of the alkali balance which clearly showed that the addition of CaCl_2 does enhance alkali volatility. The author also pointed out that the CaCl_2 acted as a mineralizing agent, aiding clinker burning and reducing kiln dust loading somewhat. However, these advantages will not necessarily apply to modern preheater kiln systems, because of the much greater degree of capture of alkalis in the preheater, and subsequent "plugging" problems brought on by the CaCl_2 .

An Italian paper⁽⁴⁾, for which we have only the abstract, provides confirmation that CaO tends to displace alkalis from their combination with silica and alumina at high temperatures, and thus, minerals such as leucite, $(\text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot 4\text{SiO}_2)$, react with CaO to give $\beta\text{-C}_2\text{S}$ and also calcium aluminates at temperatures above 1050°C . The fate of the potassium is not clear, although the author notes that the additions of CaCl_2 , CaF_2 or Fe_2O_3 favor the reaction. Presumably, they act as mineralizers.

A paper by Hastrup⁽⁵⁾ deals specifically with a problem which may arise in precalciner kilns, namely, blockage of the lower two cyclones due to recarbonation of CaO . In the CO_2 -rich atmosphere produced by the precalciner, CaO , which initially adheres to the cyclone walls due to the presence of traces of low-melting alkali salts⁽⁶⁾, can recarbonate if it is present in a lower temperature zone than the calcining zone itself. This recarbonation occurs with a considerable increase in volume, which gives rise to a hard deposit on the walls of the cyclones. The problem is generally most serious if pure

CaCO_3 is used in the kiln feed; (this may be because impure CaCO_3 tends to form calcium silicates, aluminates and ferrites which tend not to recarbonate readily). Clearly, this suggests that care must be taken when designing a "separate argillaceous precalciner" kiln in which the limestone and argillaceous components will pass through separate preheater systems.

Hastrup⁽⁵⁾ also draws attention to the fact that the rate of calcination is inversely dependent on the size of the CaCO_3 particles, i.e., that larger CaCO_3 particles take longer to fully decompose to CaO . This is an important point in the design considerations for any precalciner. Hastrup points out that, if the gases are moving upwards in the calcining zone, the effective residence time of the larger particles will be longer, which will help to counteract their slower calcination rate.

Russemeyer⁽⁷⁾ discusses the conversion of a Buehler-Miag preheater kiln to precalcining by the installation of a burner into the riser duct. He found that such an installation could give rise to problems, especially those connected with alkali chlorides. The contents of K_2O and Cl in the bypass dust actually dropped quite markedly (by about a factor of three) during precalcination. Russmeyer attributed this to the reduction in kiln exit gas temperature resulting from the decrease in kiln fuel consumption. Clearly, the use of a precalciner in this system also necessitates a shortening of the

rotary kiln in order to take full advantage of the bypass for removing alkali salts.

Useful information on the design and operation of conventional precalciner kilns is available in the literature. Rechmeier⁽⁸⁾ describes an early precalciner design for burning oil shale as part of the raw mix. The kiln was a 4-stage suspension preheater modified by the addition of a vertical precalcining shaft and a fifth cyclone. Rapid combustion of the oil shale was achieved by injecting it into the shaft, where hot kiln exit gases and preheated air from the clinker cooler mix. Complete combustion of the oil shale was achieved in under 1.5 seconds; the shale ash also mixed well with the remaining raw feed ingredients. Ring formation in the kiln due to excess sulfur from the shale was minimized by increasing the kiln speed and the silica modulus of the raw mix.

A paper by Kobayashi⁽⁹⁾ gives much useful information regarding the design of the flash-furnace used in the IHI (Ishikawajima-Harima Heavy Industries) "SF" precalciner kiln. The flash furnace is designed in two sections, the lower of which creates a vortex in the hot gases which enter from the base of the furnace, thereby ensuring a high degree of cylindrical symmetry in the temperature profile of the furnace. Both fuel and kiln feed are injected downwards from the top of the furnace. Another paper by Mori et al⁽¹⁰⁾ gives useful information on the design of another successful Japanese precalciner kiln system, namely the Onoda "RSP" process, which differs from the IHI-SF process in that the burner section of

the precalciner is separate from the calcining zone, and, furthermore, the precalciner gases plus calcined raw feed do not mix with the kiln exit gases until after the bulk of the calcination has taken place. Further discussion of these and other precalciner systems can be found with PCA report on Energy Conservation⁽¹¹⁾. All of this information may be useful when it comes to designing a suitable precalciner for the "separate argillaceous precalciner" system proposed in this work.

2. On-Line Gas Analysis

The possibility of a continuous, on-line system for analyzing the kiln- or precalciner-exit gas stream for the major "volatile" components of kiln feed, (i.e., alkalies, sulfur and chlorine), was raised in the original proposal. Ideally, such a system would have to be capable of analyzing a dusty gas stream, because in most cases the alkalies will be present in the form of solid or liquid alkali sulfates or chlorides suspended in the gas. This is inevitable because the boiling points of most of the common alkali salts are above 1300°C. In order to ensure complete vaporization of alkali salts, the gas stream should probably be at a temperature in excess of about 2000°C, which would present severe problems in handling. The alternative is to sample the gas stream at a lower temperature, but taking care not lose any particulates (e.g., use isokinetic sampling techniques). In this case it might be best to "chill" the gas to below about 700°C, to ensure that no liquid phase is present, which could otherwise cause blockage

of the sampling tubes. If the particulates can be maintained in gaseous suspension, they might then be analyzed by use of a plasma spectrograph^(12,13).

At present, the development of plasma spectroscopy for the analysis of dusty gases is at a preliminary stage⁽¹²⁾, but it is hoped that volatile elements, such as Na, K, S and Cl, (which are of special interest to us), will be susceptible to this type of analysis in the near future. Other, less volatile elements such as Ca, Al, Si and Fe, will present more serious problems. Nevertheless we will continue to search the literature for any information on progress in this field. It does appear, at present, that plasma spectroscopy is likely to be the most suitable method for this type of analysis. Once the elements have been vaporized, they may be monitored in the gas phase (sometimes even as ions) by emission or absorption spectrometry⁽¹³⁾. No other method is capable of analyzing all these elements in total, although there are well known methods for analyzing for various gaseous sulfur compounds such as H_2S , SO_2 and SO_3 which may also be present in any kiln exit gas stream. These gases may be analyzed by chemical methods, by I.R. or U.V. absorption spectrometry, and various other methods, and the equipment is already commercially available.

3. Pure Minerals - Alkali Vaporization Studies

The work described in the first quarterly report (Aug.-Oct. 1978) was continued, using similar experimental techniques, with some modifications. Two sets of additives were tried, namely:

(1) CaCO_3 and $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$

(2) MgCl_2 and NH_4Cl

3.1 Burns Using a Calcium Carbonate/Calcium Chloride Combination

The results in the previous report showed clearly that the addition of calcium chloride, (CaCl_2), enhanced the vaporization of alkalis from most of the pure mineral samples. The best results had been obtained with the albite, muscovite and microcline, which had the highest initial alkali content. However, the results were not as good as might have been hoped; in no case was more than about 35% of the total alkali content of the mineral volatilized, even at 1100°C . Therefore, it was decided to try the combined addition of CaCl_2 and CaCO_3 , with the hope that the extra CaO made available, (by the decomposition of CaCO_3 at $800\text{--}900^\circ\text{C}$ to $\text{CaO} + \text{CO}_2$ gas), would help replace alkali metal ions in the alumino-silicate structure of the various minerals, and thus increase the tendency of the alkalis to vaporize.

Six mixes were made up using each of the pure minerals (100 parts), and varying additions of CaCl_2 (in the form of the dihydrate, $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$). The quantity of CaCl_2 added was such that it provided the correct quantity of chloride anion to combine with the total amount of sodium and potassium cations in the pure mineral.

The mixes were made up by intergrinding in a dry atmosphere (relative humidity 10-12% at about 70°F), in order to minimise the absorption of atmospheric water by the samples. This method

appeared to work as well as, if not better than, the wet mixing method used in the previous tests. Furthermore, the actual ignition losses of the mixes were measured during several of the burns (all those burns involving a thin-layer sample at 100°C). This gave an accurate means of calculating the true amount of alkali volatilized during the burn. It could be assumed, with only a small degree of error, that the total ignition loss of thin-layer and pellet samples at both 1000°C and 1100°C would be the same.

The results of the 24 burns on these six mixes are given in Table 1. All burns were of one half hour duration, as in the previous tests. The initial mix was analyzed directly for alkali content. This alkali content, corrected for the observed L.O.I. at 1000°C, is also given in the table and this figure can be used for direct comparison with the alkali contents of the ignited products. The observed percentage reductions in alkalies are also given in the table. In cases where increases in alkali content were observed, the numbers are bracketed.

The results show clearly that the addition of 20% CaCO_3 increases the degree of alkali volatilization especially from the albite, muscovite, microcline and illite, (in other words, those minerals which have the highest alkali contents). The alkali loss generally increases slightly from 1000°C to 1100°C and from pellet to thin-layer burns, but the 1000° pellet burns on the muscovite and illite, and the 1100° pellet burn on the microcline, show higher-than-expected alkali losses. Although these results are better than the results with CaCl_2 alone, the

total fraction of the initial alkali content volatilized from any one mix is seldom greater than about one half. In the case of the two feldspars, (albite and microcline), it is notable that the less abundant alkali, (i.e. potassium in the albite, sodium in the microcline) almost always appears to be more volatile. The reverse appears to be true for the muscovite and illite, where the more abundant alkali, (which is potassium in both cases), is usually the more volatile. These trends are shown more clearly in these results than in the first set of results with only CaCl_2 additions (in the previous report).

It is notable that, in all cases, the kaolin mix shows gains in sodium and potassium content, and the montmorillonite shows gains in its potassium content. It seems likely that these are real effects, and not just due to experimental error. These gains in alkali content could well be due to condensation of alkali vapor during the burn, because in all cases the burns were carried out on three samples simultaneously in the same furnace. The sets of three were made up in the order shown in Table 1, i.e. (i) kaolin, albite, muscovite, and (ii) montmorillonite, microcline and illite. Thus, in set (i), albite releases a large amount of sodium into the vapor phase, whereas muscovite releases a large amount of potassium; (presumably both are in the form of chlorides), providing a kiln atmosphere in which the vapor pressure of the alkali compounds may exceed their equilibrium vapor pressure over kaolin, thus causing some "condensation" which may in fact involve a reaction with the

kaolin decomposition products. In the case of the montmorillonite, the kiln atmosphere is likely to contain mainly potassium as microcline and illite contain little sodium; this corresponds with the gain in potassium content shown by the montmorillonite. In any case, montmorillonite itself contains considerably more sodium than potassium. This tentative explanation will be tested by more careful experiments in future, where the mixes will be burned separately. (We hope to be able to conduct these burns in our new tube furnace, which should be available shortly). The use of a tube furnace is desirable, since a current of gas can be drawn over the surface of the sample during heating, which should ensure rapid removal of any vapors.

In view of these rather interesting results, it was decided to determine the loss of alkali vs. time for the two feldspars, since we at present have little information on the rate at which the alkalis are being vaporized. Burns of the same mix used in the tests in Table 1 were made on thin-layer specimens at 1000°C for 15 mins, 30 mins, 1 hour and 2 hours. The results are given in Table 2, and are shown graphically in Figure 1; the initial value being the alkali content of the unignited mix corrected for the observed L.O.I. as shown in Table 1.

It is clear, from the curves in Figure 1, that the alkali contents of the two feldspars decreases most rapidly during the first half hour, but appears to be tending towards a steady "equilibrium" value after about one hour. It is also clear that, as observed earlier, the least abundant alkali is lost

more rapidly (on a fractional basis), at least in the first half-hour.

The fact that the alkali loss does tend towards a limit is of considerable interest, since this indicates that there may be some equilibrium factor which determines the limit; in other words, the equilibrium situation may be one in which not all the alkali is lost from the sample. Of course, one must be careful when talking about equilibria in experiments such as these, because theoretically the equilibrium will always depend on the partial pressure of the alkalies present in the vapor phase. Nevertheless, to all intents the results indicate that some sort of "pseudo-equilibrium" is being reached in these experiments. It may be that this "pseudo-equilibrium" is influenced by the rate at which alkali chlorides can diffuse out of the furnace; this will be tested in future by carrying out the burns in a flowing gas stream (in a tube furnace).

3.2 Burns Using a Magnesium Chloride/Ammonium Chloride Combination

The original intention expressed in the research proposal was to try the addition of MgCl_2 as a source of chlorine for alkali vaporization. However, due to the deliquescent nature of MgCl_2 , it is difficult to prepare it free of water. Any attempt to completely dehydrate the hexahydrate, $(\text{MgCl}_2 \cdot 6\text{H}_2\text{O})$ by heating in air leads to loss of HCl and formation of an oxy-chloride. In order to avoid this, we mixed approximately equal amounts of $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ and NH_4Cl , and heated the mix for over a day at 250°C to remove the water. The resulting solid was not

analyzed fully, but presumably contained a mixture of anhydrous MgCl_2 and NH_4Cl . The ignition loss of the dry solid was determined to be 70.0% at 1000°C . The residue, after ignition, was dissolved and the solution analyzed for chloride using a "Quantab" indicator. The calculated chloride content of the residue was 73.4% with a probable error of about $\pm 3\%$; i.e. within experimental error the ignited residue had the same chloride content as pure MgCl_2 (which contains 74.47% chloride). Therefore, the amount of the dry $\text{MgCl}_2/\text{NH}_4\text{Cl}$ mixture which was to be added to the pure mineral in each case was calculated on the basis of equivalence between the remaining chloride content at 1000°C and the alkali content of the pure mineral. Mixes of the pure minerals with $\text{MgCl}_2/\text{NH}_4\text{Cl}$ were prepared in a dry atmosphere, and were burned as thin-layer specimens at 1000°C for one half-hour, and the resulting products analyzed for alkali content, as shown in Table 3. The actual loss-on-ignition during each of the runs was determined and is compared with the values which would be expected if the alkali loss were due to vaporization of NaCl and KCl . As before, the burns were made (in platinum dishes) in two groups of three, and this may again help to explain the observed increase in alkali content of the kaolin and montmorillonite, which is thought to be due to condensation of alkali salts* (as dis-

*Note: As a test of this hypothesis, the kaolin/ $\text{MgCl}_2/\text{NH}_4\text{Cl}$ mix was burned on its own for 1/2 hour at 1000°C , giving a product containing 0.040% Na_2O and 0.128% K_2O . If these results are compared with those in Table 3, it can be seen that a small that that a small reduction in both alkalies has occurred, confirming that the kaolin does lose alkalies under these conditions, if no excess alkali vapors are present in the furnace atmosphere.

cussed in Section 3.1). All the other minerals showed a loss in alkali, except for the potassium content of the illite, (which again behaved similarly to the results obtain with $\text{CaCO}_3/\text{CaCl}_2$ mixes as shown in Table 1). The two feldspars again showed the greatest degree of alkali loss, the albite losing 42.9% of its original alkali content, and the microcline losing 35.6%. Again, both feldspars lost a higher fractional amount of their least abundant alkali. Interestingly, the same was also true for the muscovite and illite, which both lost more of their sodium than of their potassium; this was the reverse of their behaviour in the $\text{CaCO}_3/\text{CaCl}_2$ burns. The muscovite burns with $\text{MgCl}_2/\text{NH}_4\text{Cl}$ showed a similar degree of alkali volatilization at 1000°C to the burns made with only CaCl_2 additions (see previous report), but the muscovite lost much more alkali in the $\text{CaCO}_3/\text{CaCl}_2$ burns. This does suggest that the presence of excess CaO aids alkali volatilization from the muscovite. This trend was not observed as clearly for any of the other minerals; the feldspars actually lost more alkali at 1000°C with the $\text{MgCl}_2/\text{NH}_4\text{Cl}$ mix than they did with the $\text{CaCO}_3/\text{CaCl}_2$ mix at the same temperature. This suggests that there is a definite difference in both the mechanism and the thermodynamics of alkali volatilization between the feldspars and the muscovite. The illite behaves very oddly in all cases, sometimes gaining potassium but losing sodium.

3.3 Vaporization Studies: Discussion of Results So Far

The major conclusions which can be drawn from the pure mineral alkali-vaporization studies so far are that:

- (i) The presence of excess CaO aids volatilization of alkali from the muscovite and illite, but does not exert such a strong influence on the feldspars.
- (ii) Thin layer samples usually, but not always, lose more alkali than pellets (as would be expected due to their higher surface area).
- (iii) The rate of alkali loss (of the feldspars) decreases with time and appears to tend towards a limiting value.
- (iv) The low-alkali minerals (kaolin and montmorillonite) tend to absorb alkalis from the vapor phase under our existing experimental conditions.

This last point suggests that we should carry out all future burns using only one sample at a time, preferably using a tube furnace and passing a current of gas over the sample. We had intended to use this method, in any case, for vaporization studies in a controlled atmosphere.

As well as the major observations noted above, it is also apparent, from the results in Tables 1 and 3, that the observed loss-on-ignition of the samples is usually appreciably greater than the expected L.O.I. calculated on the basis of the known L.O.I.'s of the components in the mix, even when loss of alkali chlorides is taken into account. This is especially true for the feldspars and the muscovite; however, the kaolin actually shows a lower-than-expected L.O.I.

This observation might, of course, be attributed to excess moisture present in the mixes before ignition. To test for this more thoroughly, three further test burns were made on the

albite, muscovite and microcline. In each case, the L.O.I. of the mixture with $\text{CaCO}_3/\text{CaCl}_2$ used in 3.1 (Table 1) was measured after heating for one hour at about 350°C , i.e. a temperature high enough to ensure complete dehydration of the CaCl_2 . The mixture was then heated to 1000°C for one half-hour, and the L.O.I was again determined. The L.O.I. of the pure minerals alone at 350°C were also determined. These results were used to calculate and compare the observed and predicted L.O.I's of the mixes at 350° and 1000°C , on the assumption that the L.O.I.'s of the individual components in the mixes behaved additively, and the loss of alkali observed at 1000°C was due to vaporization of NaCl and KCl only. The results of this study are given in Table 4. It is clear, from Table 4, that there is a small discrepancy between the observed and calculated L.O.I.'s at 350°C in all cases - this discrepancy was approximately proportional to the amount of CaCl_2 present in each sample, and can presumably be attributed to a slight excess of water due to deliquescence of the $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$. However, the results also show appreciable discrepancies between the calculated and observed L.O.I's at 1000°C , which cannot now be attributed to water loss, and so must be due to loss of some compound other than H_2O , CO_2 , NaCl or KCl . Since NaCl and KCl are the "heaviest" compounds (on a molecular weight basis) of the alkalis which are likely to have volatilized, it seems certain that the extra weight loss is due to some non-alkali compound, and the two most likely candidates are AlCl_3 and

FeCl_3 , both of which are known to be extremely volatile in their pure states.

Interestingly, a paper by Russian workers, (1), covered in our literature survey, contains evidence that FeCl_3 is lost from a cement raw mix in the kiln when alkali chlorides or alkaline-earth chlorides are added. However, it is not at present clear how these workers determined the degree of iron loss; we are presently awaiting a full translation of this paper. There is apparently very little available information on the reactions between alkali alumino-silicates and chloride salts at high temperatures. We plan, therefore, to carry out a further literature search in this area. We also hope to be able to obtain some thermodynamic data which will help us in predicting the likely positions of equilibria in the various systems.

With regard to existing experimental data on the alkali chlorides, alkaline-earth chlorides and also AlCl_3 and FeCl_3 , Mellor's Treatise on Inorganic Chemistry (14) is still an invaluable reference source. According to this treatise, AlCl_3 sublimes at 183°C to give a vapor mainly composed of Al_2Cl_6 molecules. Similarly, FeCl_3 boils at 315°C to give a vapor mainly composed of Fe_2Cl_6 molecules. Fe_2Cl_6 begins to dissociate appreciably above 500°C , and above 750°C the vapor is almost entirely composed of FeCl_3 molecules. In the absence of excess chlorine vapor, FeCl_3 tends to dissociate to give Fe_2Cl_4 vapor, such that the partial pressure of Cl_2 in equilibrium with Fe_2Cl_6 vapor (at 1 atmosphere total pressure) is

about 0.1 atmosphere at 500°C. Ferrous chloride (FeCl_2) boils at about 1023°C; the vapor contains Fe_2Cl_4 molecules, especially at low temperatures, as well as FeCl_2 molecules. Similarly, Al_2Cl_6 is stable at lower temperatures, but above 800°C the vapor is mainly AlCl_3 . However, the high volatility of AlCl_3 and FeCl_3 in the pure state does not necessarily extend to their related compounds. For example, NaCl reacts with AlCl_3 to form various chloroaluminates, e.g. NaAlCl_4 , which are relatively stable and do not lose AlCl_3 vapor appreciably below "white heat", although they do sublime unchanged at these high temperatures. It is not clear if the vapor phase consists of separate NaCl and AlCl_3 molecules, or NaAlCl_4 complex molecules. KCl also forms similar complexes.

A further consideration is the effect of the atmosphere on the chlorides. The following equilibrium:

tends to move to the right hand side at lower temperatures, although reaction is slow. However, this reaction may in part be responsible for the loss of chlorine which has been observed when a mixture of NaCl and Al_2O_3 is heated in air (14); the product would presumably be a sodium aluminate. In the presence of water vapor, the decomposition of AlCl_3 is fairly rapid, even at high temperatures:

There is some evidence that aluminosilicates can react with alkali chlorides to form AlCl_3 (Ref. 14, Vol V). When certain clays are heated together with NaCl and carbon, NaAlCl_4 may

be formed. This reaction is enhanced by the presence of chlorine in the gas phase; even SiCl_4 may be formed under some circumstances. The carbon in the mixture acts as a reducing agent to remove oxygen; thus the basic reaction is presumably:

The alkali-chloroaluminate system tends to produce very low melting-point mixtures; apparently, the ternary eutectic is 14 mole % KCl , 26 mole % NaCl and 60 mole % AlCl_3 , with a melting point of only 93°C . The presence of traces of AlCl_3 vapor together with solid alkali chlorides may, therefore, be responsible in some cases for melt formation associated with cement kiln systems at very low temperatures. However, the AlCl_3 would be unstable if any appreciable amount of water vapor were present in the atmosphere.

The form of the alkali chlorides in the vapor phase is of interest in this study. There is evidence that NaCl is associated into Na_2Cl_2 molecules at lower temperatures; the dissociation energy of Na_2Cl_2 is reported to be about 43 kcal/mole, which suggests that the molecule will dissociate fully at temperature above 600°C or so. NaCl itself boils at 1473°C at 1 atmosphere pressure, and has a vapor pressure of about 0.023 atmospheres at 1000°C . KCl has a vapor pressure of about 0.021 atmospheres at 1000°C , but boils at 1411°C ; this suggests that NaCl is more volatile than KCl at temperatures below about 1000°C , but less so at higher temperatures. (However, not all this data is necessarily reliable; there are often discrepancies between the various workers cited in reference 14).

The degree of dissociation of the alkali halides into atoms is also significant; one reference quoted in (14) states that KCl vapor is 0.002% dissociated at 550°C, whereas another reference states that the heat of dissociation of KCl is 101.2 kcal/mole, which suggests that much less than 0.002% dissociation would be observed at 550°C, and temperatures in excess of 2000°C would be required to achieve an appreciable degree of dissociation. Further references concur with this view, and no appreciable dissociation of NaCl or KCl vapor into atoms or ions is reported at 2000°C.

Clearly, there is considerable scope for further, more careful literature surveying in the area of the thermodynamics of the alkali volatilization process. We hope to be able to obtain and tabulate the latest thermodynamic data and use these results for comparison with our experimental data by the next quarterly report on this project.

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Volumes of interest for this study:
 Vol. 11 (K, Na and Cl)
 Vol. V (Al)
 Vol XII, XIII and XIV (Fe)

Figure 1: Alkali content vs. time at 1000°C (thin-layer)
for mixes of feldspars, CaCO_3 and $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$.

TABLE 1 - ALKALI LOSS FROM PURE MINERALS WITH CaCO_3 AND $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$

Pure Mineral (to which 20% extra CaCO_3 was added)	Weight of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ added, per 100 Units of Pure Mineral	Calculated* L.O.I. if No Alkali Volatil- ized, %	Observed L.O.I. of thin- layer at 1000° C %	Alkali Oxide	Initial alkali content of mix, %	Initial alkali content of mix cor- rected for observed L.O.I., %	Type of Run							
							1000° Thin Layer		1000° Pellet		1100° Thin Layer		1100° Pellet	
							Alkali in Product, % as Oxide	Alkali Volatil- ized, as % of Original Alkali	Alkali in Product, % as Oxide	Alkali Volatil- ized, as % of Original Alkali	Alkali in Product, % as Oxide	Alkali Volatil- ized, as % of Original Alkali	Alkali in Product, % as Oxide	Alkali Volatil- ized, as % of Original Alkali
PDC 155: Kaolin	0.35	19.19	19.02	Na_2O	0.04	0.05	(0.06)	--	(0.08)	--	(0.14)	--	(0.07)	--
				K_2O	0.10	0.13	(0.26)	--	(0.14)	--	(0.19)	--	(0.16)	--
PDC 156: Albite	28.9	11.85	20.21	Na_2O	7.28	9.12	6.49	28.8	7.18	21.3	4.75	47.9	4.79	47.5
				K_2O	1.00	1.25	0.55	56.0	0.99	20.8	0.23	81.6	0.37	71.2
PDC 157: (Mica) Muscovite	17.5	14.38	21.23	Na_2O	0.50	0.63	0.46	27.0	0.45	28.6	0.53	15.9	0.46	27.0
				K_2O	7.24	9.19	4.85	47.2	3.16	65.6	4.16	54.7	5.21	43.3
PDC 158: Montmoril- lonite	5.5	20.68	20.10	Na_2O	1.65	2.07	1.95	5.8	(2.12)	--	1.83	11.6	1.98	4.3
				K_2O	0.45	0.56	(0.57)	--	(0.57)	--	(0.57)	--	(0.60)	--
PDC 168: Microcline	23.5	10.51	20.68	Na_2O	1.45	1.83	1.17	36.1	1.55	15.3	1.04	43.2	0.96	47.5
				K_2O	8.00	10.09	6.87	31.9	8.44	16.4	6.74	33.2	6.35	37.1

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TABLE 1 - ALKALI LOSS FROM PURE MINERALS WITH CaCO_3 AND $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$

(Continued)

Pure Mineral (to which 20% extra CaCO_3 was added)	Weight of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ added, per 100 Units of Pure Mineral	Calculated* L.O.I. if No Alkali Volatil- ized, %	Observed L.O.I. of thin- layer at 1000° C %	Alkali Oxide	Initial Alkali Content of mix, %	Initial Alkali Content of mix cor- rected for observed L.O.I., %	Type of Run							
							1000° Thin Layer		1000° Pellet		1100° Thin Layer		1100° Pellet	
							Alkali in Product, % as Oxide	Alkali Volatil- ized, as % of Original Alkali	Alkali in Product, % as Oxide	Alkali Volatil- ized, as % of Original Alkali	Alkali in Product, % as Oxide	Alkali Volatil- ized, as % of Original Alkali	Alkali in Product, % as Oxide	Alkali Volatil- ized, as % of Original Alkali
PDC 169: Illite	7.8	17.60	20.26	Na_2O	0.43	0.54	0.43	20.4	0.46	14.8	0.49	9.3	0.44	18.5
				K_2O	3.15	3.95	3.04	23.0	(4.78)	—	2.65	32.9	2.66	32.7

*This is calculated simply on the assumption that the L.O.I. of the pure mineral will be unaltered, and that CaCO_3 and $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ will be converted to CaO and CaCl_2 , respectively. Any loss of alkali (e.g. as chloride), will increase the observed L.O.I. above this value.

Table 2: Alkali Loss of Feldspar/CaCO₃/CaCl₂·2H₂O Mixes vs.

Time at 1000°C, for Thin-Layer Samples

Mix:	Albite CaCO ₃ CaCl ₂ ·2H ₂ O	(100 parts) (20 parts) (28.9 parts)	Microcline (100 parts) CaCO ₃ (20 parts) CaCl ₂ ·2H ₂ O (23.5 parts)			
	Na ₂ O	K ₂ O	Total Na ₂ O Equivalent	Na ₂ O	K ₂ O	Total Na ₂ O Equivalent
Initial alkali content of mix, weight %:	7.28	1.00	7.94	1.45	8.00	6.71
Initial alkali content of mix, corrected for observed L.O.I. at 1000°C:	9.12	1.25	9.94	1.83	10.09	8.47
Observed alkali content of product, % by weight, after burning for:						
15 min.	7.74	1.06	8.44	1.57	8.42	7.11
30 min.	6.49	0.55	6.85	1.17	6.87	5.69
60 min.	5.60	0.39	5.86	0.84	6.30	4.99
120 min.	5.13	0.15	5.23	1.28	6.39	5.48
Alkali contents of initial mix and pro- ducts, relative to the initial weight of the pure mineral present:						
Initially:	10.84	1.49	11.82	2.08	11.48	9.64
15 min.	9.20	1.26	10.03	1.79	9.58	8.09
30 min.	7.71	0.65	8.14	1.33	7.82	6.47
60 min.	6.66	0.46	6.96	0.96	7.17	5.68
120 min.	6.09	0.18	6.21	1.46	7.27	6.23

TABLE 3 - ALKALI LOSS FROM PURE MINERALS WITH $\text{MgCl}_2/\text{NH}_4\text{Cl}$

Pure Mineral	Weight of $\text{MgCl}_2/\text{NH}_4\text{Cl}$ * added, per 100 units of pure mineral	Calculated** L.O.I., if No Alkali Chlorides Volatilized, %	Observed L.O.I. at 1000°C %	Alkali Oxide	Initial Alkali Content of Mix, % (Calculated)	Initial Alkali Content of Mix, Corrected for Observed L.O.I., %	1000°C Thin-Layer Burn		Change in Weight due to Alkali as Chloride, %	***Calculated L.O.I. corrected for loss of Alkali as Chloride
PDC 155: Kaolin	0.804	14.65	14.05	Na_2O	0.06	0.07	(0.13)	(-85.7)	+0.097	14.48
				K_2O	0.13	0.15	(0.20)	(-33.3)	+0.069	
PDC 156: Albite	64.52	28.52	38.69	Na_2O	7.22	11.78	7.06	40.1	-5.46	35.06
				K_2O	1.11	1.81	0.70	61.3	-1.08	
PDC 157: (Mica) Muscovite	37.62	23.01	29.43	Na_2O	0.48	0.68	0.56	17.6	-0.16	24.18
				K_2O	7.15	10.13	9.23	8.9	-1.01	
PDC 158: Montmorillonite	12.25	21.72	22.83	Na_2O	1.72	2.23	(2.32)	(-4.0)	+0.13	21.31
				K_2O	0.50	0.65	(0.88)	(-35.4)	+0.28	
PDC 168: Microcline	52.45	24.42	36.10	Na_2O	1.50	2.35	1.31	44.3	-1.25	30.10
				K_2O	8.24	12.90	8.52	34.0	-4.43	

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TABLE 3 - ALKALI LOSS FROM PURE MINERALS WITH $\text{MgCl}_2/\text{NH}_4\text{Cl}$

(Continued)

Pure Mineral	Weight of $\text{MgCl}_2/\text{NH}_4\text{Cl}$ * added, per 100 units of pure mineral	Calculated** L.O.I., if No Alkali Chlorides Volatilized %	Observed L.O.I. at 1000°C %	Alkali Oxide	Initial Alkali Content of Mix, % (Calculated)	Initial Alkali Content of Mix, Corrected for Observed L.O.I., %	1000°C Thin-Layer Burn		Change in Weight due to Alkali as Chloride, %	***Calculated L.O.I. corrected for loss of Alkali as Chloride
							Alkali in Product, % as Oxide	% of Original Alkali Volatilized		
PDC 169: Illite	17.32	20.38	23.76	Na_2O	0.55	0.72	0.57	20.8	-0.22	20.48
				K_2O	3.41	4.47	(4.57)	(-2.2)	+0.12	

*This was an anhydrous mixture of MgCl_2 and NH_4Cl , which had a loss-on-ignition of 70.0%. The ignited residue contained 73.4% Cl^- , and was added to the pure mineral on the basis of residual chloride equivalence to the alkali content.

**This L.O.I. was calculated from the combined L.O.I. of the mineral plus the additive. Any loss of alkali (as chloride), would increase the L.O.I. above this value.

***This L.O.I. was calculated on the assumption that all the loss of alkali occurred via vaporization of alkali chloride. Any increase in alkali is assumed to be due to condensation of alkali chloride.

TABLE 4 - L.O.I. MEASUREMENTS FOR THREE PURE MINERAL MIXES

Mix:	PDC 156 (Albite), CaCO ₃ , CaCl ₂ ·2H ₂ O	PDC 157 (Muscovite), CaCO ₃ , CaCl ₂ · 2H ₂ O	PDC 168 (Microcline), CaCO ₃ , CaCl ₂ ·2H ₂ O
Proportions:	100:20:28.9	100:20:17.5	100:20:23.5
L.O.I. of pure mineral at 350°C, 1 hour	0.69%	0.86%	0.18%
Observed L.O.I. of mix at 350°C, 1 hour	7.26%	5.21%	6.02%
Calculated L.O.I.* of mix at 350°C	5.19%	3.73%	4.12%
Discrepancy at 350°C	+2.07%	+1.48%	+1.90%
Observed L.O.I. on heating from 350°C to 1000°C and holding at 1000° for 1/2 hour, (relative to initial "cold" weight)	12.14%	17.30%	15.77%
Expected L.O.I. between 350° and 1000°C**	11.31%	14.45%	11.35%
Discrepancy at 1000°C	+0.83%	+2.85%	+4.42%

*L.O.I. at 350°C calculated on the assumption that all the water from the CaCl₂ hydrate is lost, together with the normal L.O.I. for the pure mineral at this temperature.

**L.O.I. at 1000°C is calculated on the assumption that the L.O.I. for the pure mineral itself at 950°, (corrected to zero alkali loss), can be used, in addition to the L.O.I. for CaCO₃ (total decarbonation), plus a further L.O.I. calculated from the observed loss of alkali (as shown in Table 1) on the assumption that all alkali losses are in the form of the chlorides.

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