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FLUXING REACTIONS OF SULFATES AND CARBONATES IN CEMENT CLINKERING II. THE SYSTEM $CaCO_3$-K_2CO_3

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Abstract

The title system has been investigated using 25 compositions. Three solid binary phases were encountered: $CaK_2(CO_3)_2$, $Ca_2K_2(SO_4)_3$ and a third having the most probable composition $2K_2SO_4 \cdot 5CaCO_3$. Three eutectics were located by thermal methods. In a CO_2 atmosphere at 1 bar pressure, melts did not lose significant CO_2.

INTRODUCTION

In modern cement clinkering processes, the blended components of the clinker meal are subject to a two-stage pyroprocessing. In the first stage, in the suspension preheater, numerous reactions occur amongst the carbonates, sulfates, etc. The second stage, the rotary kiln, operates at sufficiently high temperature to partially fuse the clinker. However, the complex countercurrent circulation of hot gas and solid leads to transfer of volatiles between stages. The species transported include alkali sulfates and carbonates, which have low melting points as well as high vapour pressures. Some of the phase relations amongst sulfates and carbonates have been reviewed in the first part of this paper (1). We now report on phase relations between calcium and potassium carbonates.

PREVIOUS STUDIES

This system was first studied by Niggli (2) who obtained data up to 60 mol % $CaCO_3$ and determined the congruent melting point of $CaK_2(CO_3)_2$ as 815°C. Solid solution of $CaCO_3$ in K_2CO_3 was encountered, extending to 15 mol % $CaCO_3$.

Kroger et al. (3) reexamined the system at 50 bars CO_2 pressure which enabled the range of compositions studied to be extended without decomposition to 80 mol % $CaCO_3$. A second binary phase, $K_2Ca_2(CO_3)_3$, was determined; it was stable to 835°C, but its melting behaviour remained uncertain. Malik et al (4) and Chatteraj et al. (5) investigated parts of the system by thermal analyses; even 1% K_2CO_3 was found to depress the decomposition temperatures of $CaCO_3$ by *ca* 35°C.

Cooper et al (6) studied the ternary system $CaCO_3$-K_2CO_3-Na_2CO_3, in the course of which they examined the K_2CO_3-$CaCO_3$ binary at 1 kbar; results are shown in Fig. 1. Solid solution of $CaCO_3$ in K_2CO_3 extended to a maximum of 11 wt % (14.5 mol %). Two intermediate compounds were observed, $K_2Ca(CO_3)_2$ and $K_2Ca_2(CO_3)_3$. The first of these, $K_2Ca(CO_3)_2$, had two polymorphs, both of which occur in nature: the high temperature polymorph, stable above 570°C, is identical with the mineral fairchildite. The low temperature polymorph was first synthesised by Büetschli (7) who grew crystals from aqueous solution: when this phase was subsequently discovered in nature, it was designated büetschliite. Its crystallography, optical properties and powder X-ray diffraction patterns have been reported by Mrose et al. (8), Swanson et al. (9) and Pabst (10). There is considerable variation, from 570° to 704°C, in the supposed equilibrium transformation temperature between fairchildite and büetschliite.

The second phase, designated phase A, is less well characterised. It has the indicated composition $K_2Ca_2(CO_3)_3$ and melts at 810°C, probably incongruently to $CaCO_3$, and also decomposes at a lower limit of thermal stability, at about 512°C, to a mixture of $CaCO_3$ and $K_2Ca(CO_3)_2$.

A wide range of carbonate melts can be obtained at 1 bar CO_2 pressure, ranging up to ~60 wt % $CaCO_3$. The liquidus is relatively flat, with melting temperatures ranging between 735° and ~810°C over a broad range of compositions.

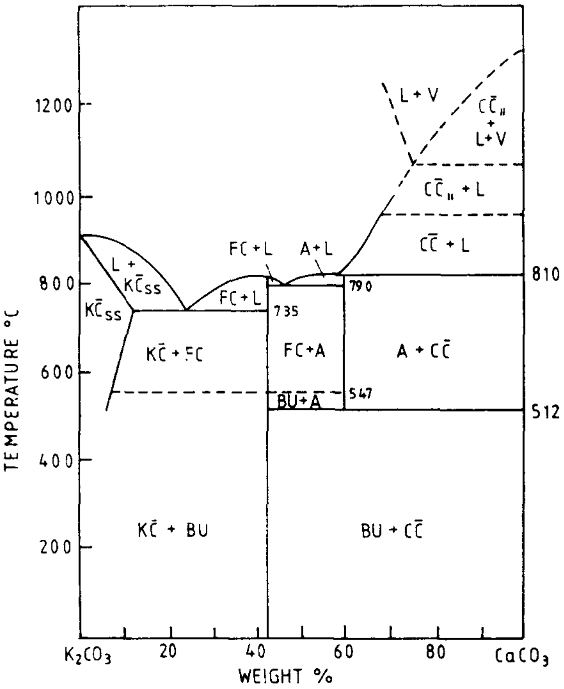

FIG. 1

The system K_2CO_3-$CaCO_3$ at 1 bar CO_2 pressure, after Cooper et al, (6)

EXPERIMENTAL

$K_2CO_3 \cdot 1.5\ H_2O$ and $CaCO_3$, both 'AnalaR' grade, were used as reactants. $CaCO_3$ was dried for 12h at 300°C and stored in a desiccator. Potassium carbonate is difficult to obtain in a form suitable for accurate weighing. Thermogravimetric analyses disclosed that the as-supplied reagent contained 12.0 wt % H_2O (theoretical for $K_2CO_3 \cdot 1.5\ H_2O$ is 15.4 wt %). However, the material in the bottle remained at a relatively stable weight, so the experimentally-determined gravimetric factor was applied to subsequent weighings of this reactant.

Weighed batches were blended in an agate mortar. They were heated in a flowing

CO_2 atmosphere at 1 bar total pressure in a horizontal tube furnace. The inert metal boats used to contain samples could be pulled to the cool end of the tube and effectively quenched while still in a CO_2 atmosphere. DTA and TGA analyses were done in a Stanton-Redcroft simultaneous apparatus, generally in CO_2 atmosphere and at a heating or cooling rate of 10° C/min. Its thermocouple was calibrated against K_2SO_4 (high-low inversion, 586°C, $KC\ell$ (melting point 770°C) and $BaSO_4$ (high-low inversions at 811° and 982°C). Solid phases were identified by X-ray powder diffraction, using a Guiner-Hägg focusing camera and CuKα radiation.

Approximately 25 compositions were prepared at composition intervals of 5% up to 50 mol % $CaCO_3$ but much more closely spaced in the range between 50 and 85 mol % $CaCO_3$: at (mol % of $CaCO_3$) 10, 15, 20, 25, 28, 30, 40, 50, 54, 58, 63. 66.2, 66.6, 67, 68, 69, 70.5, 71.2, 72.5, 75.5, 77.5, 82.3 and 85.0.

RESULTS

The results of the investigations are shown in the form of a revised phase diagram for the system, Fig.2 . Three binary phases were detected: $K_2Ca(CO_3)_2$, $K_2Ca_2(CO_3)_3$ and a phase whose composition is not completely certain, but which appears to be $2K_2CO_3 \bullet 5CaCO_3$.

At high K_2CO_3 contents, differential thermal analysis was used to verify the presence of a eutectic between K_2CO_3 and $K_2Ca(CO_3)_2$; our determinations locate it at 28 mol % $CaCO_3$ and 750°C ±2°C. We were unable to verify the reported solid solution of $CaCO_3$ in K_2CO_3; samples quenched from high temperatures were extremely hygroscopic and hydrated within minutes of being quenched. The solid solution reported in the literature is included in Fig. 2, but is dashed to show that we were unable to verify its existence in samples which were also unaffected by moisture. The fairchildite-büetscheliite inversion was encountered in a wide range of compositions upon heating; DTA gave the monotropic inversion temperature at 520°C ±3°C; the reverse reaction, on the falling temperature cycle, was not obtained by DTA but prolonged isothermal annealing of fairchildite at 500°C ±10°C yielded büetscheliite, leading to the conclusion that the equilibrium inversion temperature was > 500°C and possibly as high as 520°C.

$K_2Ca_2(CO_3)_3$ is readily prepared in phase-pure form. Thermal analyses discloses that it melts congruently at 830° ±3°C and has two polymorphic inversions, at 578 ±5°C and 805° ±5°C. Consequently, the phase diagram shows fields for the α, β and γ polymorphs of $K_2Ca_2(CO)_3$. A melt having the $K_2Ca_2(CO_3)_3$ composition is sufficiently stable in a CO_2 atmosphere to enable it to be recycled through the melting point several times without sufficient weight loss occurring to affect its apparently sharp melting. The DTA evidence therefore indicates that its melting is congruent.

One of the polymorphic phase changes in $K_2Ca(CO_3)_3$, at 518°, is close to that of the fairchildite-büetscheliite inversion temperature. However, mixtures of $K_2Ca(CO_3)_2$ and $K_2Ca_2(CO_3)_3$ gave indications of both inversions during heating although upon cooling only the inversion in $K_2Ca_2(CO_3)_3$ was encountered, as the latter is rapidly reversible at the heating and cooling rates (10°C/min.) used for thermal analyses. Cooper et al reported a lower stability limit for $K_2Ca(CO_3)_3$ at 512°C; in the present study $K_2Ca_2(CO_3)_3$ was found to persist unchanged at temperatures below its supposed lower thermal limit stability, and it is believed to persist as a stable phase to ambient temperatures.

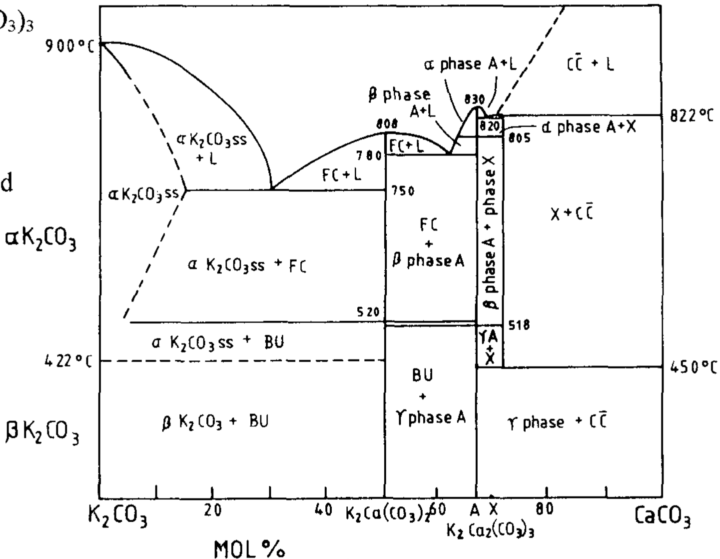

FIG. 2

The System K_2CO_3-$CaCO_3$ at 1 bar CO_2 pressure, as determined in this study. CC = calcite, FC = fairchildite, BU = büetschliite. See text for other abbreviations.

Previous workers seem not to have studied the portion of the system between $K_2Ca_2(CO_3)_3$ and $CaCO_3$ in detail. Nevertheless, the present study discloses the existence of another compound in this composition range. Cooper et al. did note possible irregularities in the slope of the liquidus in the range 66-72 mol % Ca but did not interpret these as arising from the presence of another phase. In the present study, a unique phase was reproducibly obtained in this range. It was not possible to fix the composition of the phase exactly, but the best estimate of its composition is $2K_2CO_3 \cdot 5CaCO_3$, judged from the near absence of either $CaCO_3$ or $K_2Ca_2(CO_3)_3$ reflections in X-ray patterns of fully reacted preparations at this ratio. Its melting point is ~822°C, i.e. only slightly above the temperature of its eutectic with $K_2Ca_2(CO_3)_3$. Its melting is probably incongruent, yielding`

a $CaCO_3$ as the solid phase. Upon prolonged annealing at lower temperatures it decomposes to $CaCO_3$ and $K_2Ca(CO_3)_3$ at ~ 450°C. Some dissociation occurs even on rapid cooling and it has not been possible to obtain the 2:5 phase in pure form. It is always somewhat contaminated by its solid dissociation products, $CaCO_3$ and phase A. Table 1 gives unindexed powder diffraction data for this phase, from which reflections belonging to $CaCO_3$ (calcite) and phase A have been deleted.

DISCUSSION

Taking the results of this study, together with other recent investigations of carbonate-sulfate systems, it is apparent that calcium and potassium carbonates exhibit regions of comparatively low melting point, 750° - 820° in the case of K_2CO_3 and $CaCO_3$. Moreover, such melts are relatively stable; in a CO_2 atmosphere, decomposition with loss of carbon dioxide occurs only slowly. Fluxing systems based on molten carbonates, and possibly sulfates, are potentially operative in the cooler zones of long kilns and in the suspension preheat zones of modern, energy efficient kilns. The role of low-temperature liquid formation in the ultimate production of calcium silicates is as yet unknown. But these melts have

Table 1

X-ray powder data for phase X, probably $K_2CO_3 \bullet 5CaCO_3$

d spacing, Å	I	d spacing, Å	I
7.238	8	2.425	12
7.094	11	1.875	17
6.428	5	1.862	18
3.005	100	1.830	12
2.861	26	1.800	11
2.669	21	1.732	5
2.606	16	1.525	1
2.490	33	1.297	2

CuKα radiation reflections in the range 2Θ between 10° and 75° were measured. The d spacings are relative to a KCl internal standard, for which a_0 was taken as 6.2931Å.

relatively low viscosities and surface tensions and are good solvents for a variety of oxides. Hence their transient existence during the initial stages could affect the main clinkering reactions. The existence of low melting point compositions does have another and perhaps less favourable consequence; the melts contribute to ring formation in the long rotary kiln and to particle agglomeration in suspension preheaters. The formation of low melting point eutectics with alkali salts also helps to remove alkali from kiln atmospheres. This may be desirable to control emissions, but is less desirable in limiting the alkali content of the resulting clinker.

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REFERENCES

1. Arceo, H.B. and Glasser, F.P. "Fluxing Reaction of Sulphates and Carbonates in Cement Clinkering Systems I. $CaSO_4$-K_2SO_4-$CaCO_3$", Cement and Concr. Res. 20[6] 862-868 (1990).
2. Niggli, P., "Gleichgewichte Zwischen TiO_2 and CO_2 sowie SiO_2 und CO_2 usw". Z. Anorg. Allgem. Chemie, 98 292 (1916).
3. Kroger, C., Illner, K.W. and Graeser. W "Uber die Systeme Alkalioxyd-CaO-$A\ell_2O_3$-SiO_2-CO_2. XI- Die Reactionsdrucke im System K_2O-CaO-SiO_2-CO_2", Z. Anorg. Allgem. Chemie. 251 270-84 (1943).

4. Malik, W.U., Gupta, D.R., Masood, I. and Gupta, R.S., "Kinetic Study of Thermal Decomposition of Calcium Carbonate in the Presence of K_2CO_3 and $BaCO_3$", J. Mater. Sci. (Letters) 4 532-36 (1985).
5. Chatteraj, B.D., Dutta, S.N. and Iyengar, M.S., "Studies on the Thermal Decomposition of Calcium Carbonate in the Presence of Alkali Salts (Na_2CO_3, K_2CO_3 and $NaC\ell$)", J. Thermal Analysis 5 43-549 (1973).
6. Cooper, A., Gittins, J. and Tuttle, O. F., "The System of Na_2CO_3-K_2CO_3-$CaCO_3$ at 1 Kilobar and its Significance in Carbonatite Petrogenesis", Amer. Jour. Science 275 534-560 (1975).
7. Büetschli, O., "Uber die Einwikung von konzentrierter Kalilauge und konzentrierter Losung von kohlensaurem Kali und kohlensaurem Kalk"; Verhandulgen des Naturhistorich-Medizinischem Vereins zu Heilderberg, N.F., 8 277-330 (1907).
8. Mrose, M., Rose, H. and Marinenko, J.W., "Synthesis and Properties of Fairchildite and Büetschliite: Their Relation to Wood-ash Stone Formation", Program of the Geol Soc. Am. Meeting, San Francisco. 146 (1966).
9. Swanson, H., McMurdie, H., Morris, M. and Evans, E., Standard X-ray Diffraction Powder Patterns, Nat. Bur. Stand (U.S.) Monograph 25, Sec. 8, p.48 (1970).
10. Pabst, A., "Synthesis, Properties and Structure of $K_2Ca(CO_3)_2$, Büetschliite", Am. Mineralogist 59 353-58 (1974).