A study of calcium hexaluminate

By D. S. Buist, M.A., M.Sc., Ph.D.

Central Research Laboratories, General Refractories Limited,
Worksop, Notts.

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Summary. Calcium hexaluminate has recently been confirmed as a stable phase occurring within the system $CaO–Al_2O_3$. In the present investigation, this aluminate has been synthesized from the constituent oxides and its X-ray, optical, and physical (microhardness and reflectivity) properties determined. Similar data have also been obtained on the ferrian phase from the immediate hot-face zone of high-alumina bricks that had been in service in electric arc furnace roofs. An electron-probe microanalysis study revealed that between 12 and 13 % atomic replacement of Al by Fe had occurred in this ferrian calcium hexaluminate. The melting behaviour of the pure compound has been studied by firing pellets in a specially-constructed vacuum furnace. Results show the incongruent melting point to be 1870° C (±10° C), while the liquidus temperature is 1970° C (±10° C). These points were determined by examining polished sections of compacts heated within the range 1820 to 2000° C. A revised phase diagram of the high-alumina portion of the system $CaO–Al_2O_3$ is presented.

FILONENKO (1949) first reported calcium hexaluminate as a constituent phase within the system $CaO–Al_2O_3$. A continuation of this original investigation, into the ternary system $CaO–Al_2O_3–SiO_2$, by Filonenko and Lavrov (1949) also revealed the aluminate to be a stable species. Later work by Wisnyi (1955) supported Filonenko's results. Recent work by Gentile and Foster (1963) on the high-alumina portion of the system $CaO–Al_2O_3$ and on the system anorthite–gehlenite–calcium-hexaluminate confirmed in general the results of Filonenko and Lavrov (1949), as reproduced in the Osborn–Muan diagram (1964). Despite this relatively substantial amount of evidence supporting the validity of calcium hexaluminate as a stable phase, there has been no general agreement on this point since the first phase-equilibria studies on the system $CaO–Al_2O_3$ by Shepherd, Rankin, and Wright (1909). These authors failed to identify this species, which was also omitted from the $CaO–Al_2O_3–SiO_2$ diagram of Rankin and Wright (1915). Langenberg and Chipman (1956), in their investigation of the high-alumina portion of this system, did not distinguish a primary field for this aluminate.

Calcium hexaluminate was encountered as an interfering phase in the system CaO–Al_2O_3 during an investigation of two-phase corundum–liquid bodies by the author (Buist *et al.*, 1965). Because of its obvious importance in this context, and also because of the conflicting evidence, both for and against its validity, it was decided to carry out further work on the compound. This involved synthesis of the pure material, with microscopic and X-ray investigations on it. In addition, X-ray analysis, reflectivity, and microhardness measurements were made on calcium hexaluminate developed at the immediate hot-face of a used 84 % alumina brick from the roof of an electric arc furnace. A comparison between results obtained on the latter aluminate and on the pure synthetic material has disclosed significant differences. An electron-probe microanalysis study was then made on the aluminate from the used brick to determine the factor responsible for these differences. Also, a limited investigation was carried out on the high-alumina portion of the system CaO–Al_2O_3 and the melting behaviour of the pure compound has been determined.

Synthesis. Calcium hexaluminate was prepared from the stoichiometric proportions of Analar calcined alumina (–300 B.S. mesh) and calcium carbonate. These materials were thoroughly mixed in a mechanical agate mortar, pressed into pellets at 5 ton/in^2 with a 5 % starch solution and fired for 5 hr at 1500° C in a gas furnace in air. Microscopic examination of the fired product in oils under the polarizing microscope showed that reaction had been incomplete, as a relatively high proportion of corundum was present. Pellets were then twice refired for 5 hr at 1500° C with intermediate crushing, finally producing pure calcium hexaluminate, with no free corundum remaining. Small portions of the powdered material were used for determination of optical properties under the polarizing microscope and also for X-ray diffraction studies. Pellets of the pure aluminate were somewhat friable (even after sintering for 1 hr at 1850° C in argon) and polished sections could only be obtained by the vacuum impregnation technique, using Araldite; $\frac{1}{4}\mu$ grade diamond paste was used for the final polishing.

Crystallographic and optical properties of calcium hexaluminate. The compound crystallizes in the hexagonal system and under both polarizing and mineragraphic microscopes appears as plates, which represent a combination of basal pinacoid and bipyramid (ideally, the plates are hexagonal in shape). As observed in polished section (fig. 1) there is a marked difference in relief between the aluminate and α-alumina. The optical properties of the pure synthetic calcium hexaluminate, as determined in white light, with comparative data for α-alumina and Vickers hardness data, are:

Material	ω	ϵ	*Birefringence*	*R* (%)	*V.H. No.*
Pure synthetic calcium hexaluminate* (sintered 1 h at 1850° C in argon)	1·755	1·763	0·008	7·3	985
Calcium hexaluminate (from 84 % alumina brick after service in electric arc furnace roof, English Steel Corp.)	1·762	1·769	0·007	10·5	1239
α-alumina (—300 mesh Analar alumina sintered 1 h at 1800° C in argon)	1·768	1·760	0·008	7·5	2228

Values of refractive indices ±0·002 in each case.

* Filonenko and Lavrov (1949) gave $\omega = 1{\cdot}755$, $\epsilon = 1{\cdot}762$.

X-ray diffraction study. X-ray data of the pure synthetic calcium hexaluminate and also of the variety from a used electric arc furnace roof brick were determined, using Cu-$K\alpha$ radiation with a Ni filter. The patterns were essentially similar except that the impure phase showed displacement of certain lines (see table I), indicating considerable solid solution, later shown to be mainly due to Fe_2O_3. Line shifts of approximately 0·02 Å are noted at *d* 2·774 Å. Hughes (personal communication) has confirmed this on ferrian calcium hexaluminate, obtaining line shifts of about 0·03 Å at the same *d*-spacing value. In table I, it appears unusual that the spacings of the supposedly pure standard are uniformly lower than those of the synthetic aluminate as determined during the present investigation. The radiation in both cases was Cu-$K\alpha$ and a nickel filter was used. Hughes (1967, to be published) has quoted results for the pure compound that are closely similar to those given here for the synthetic $CaO.6Al_2O_3$.

Reflectivity measurements of pure and ferrian calcium hexaluminate (with α-alumina for comparison) were made, using an eleven-stage photomultiplier (Nichol and Phillips, 1965) for a wavelength of 547 mμ against a well-polished pyrite standard (reflectivity = 53·7 %). The results are given above. These values would probably have been more accurate had a standard of comparative reflectivity been available, i.e. a neutral glass with reflectivity approximately 8 %. The actual deflection-measuring device used with the apparatus was a spot galvanometer; a digital voltmeter would have given more accurate results at these low reflectivity values.

Microhardness measurements were made using a Leitz 'Miniload' hardness tester; results are given above and are based on twelve determinations in each case.

TABLE I. X-ray diffraction patterns of pure synthetic calcium hexaluminate and of the ferrian compound from the immediate hot face of an 84 % Al_2O_3 brick from an electric arc furnace roof, English Steel Corporation, Sheffield (with standard data for comparison)

Synthetic $CaO.6Al_2O_3$		*Ferrian* $CaO.6Al_2O_3$		*Standard* (Wisnyi, 1955)	
I	*d*	*I*	*d*	I/I_1	*d*
vw	10·94 Å	vw	11·00 Å	5	10·87 Å
w	5·47	vw	5·422	10	5·507
w	4·840	w	4·755	10	4·874
w	4·408	vw	4·402	25	4·403
w	4·018	w	4·010	25	4·010
w	3·647	w	3·691	20	3·646
w	3·506	—	—	15	3·496
vw	3·239	vw	3·262	10	3·239
w	2·903	w	2·941	15	2·903
m	2·774	fs	2·790	60	2·774
w	2·748	ms	2·761	25	2·773
w	2·682	—	—	10	2·683
vs	2·623	vs	2·620	75	2·619
w	2·528	w	2·554	10	2·534
vs	4·479	s	2·501	85	2·477
f	2·406	vw	2·410	10	2·404
w	2·389	fw	2·309	15	2·380
w	2·352	—	—	35	2·346
m	2·289	m	2·311	65	2·281
b	2·207	fw	2·220	50	2·206
s	2·110 Å	m	2·101 Å	85	2·106 Å
s	2·012	fs	2·032	80	2·007
w	1·910	vw	1·942	25	1·904
vw	1·841	vw	1·825	10	1·837
w	1·806	—	—	10	1·804
m	1·711	vw	1·740	30	1·710
w	1·622	fw	1·612	20	1·617
w	1·592	—	—	20	1·605
ms	1·572	fs	1·583	70	1·570
vs	1·533	fs	1·554	85	1·533
w	1·516	w	1·522	30	1·514
—	—	vw	1·471	5	1·468
w	1·453	vw	1·432	30	1·453
vs	1·390	fs	1·401	100	1·389
m	1·312	vw	1·330	35	1·310
f	1·239	w	1·248	25	1·238
m	1·226	w	1·232	35	1·228
w	1·200	w	1·211	5	1·201
w	1·188	w	1·188	5	1·187

Electron-probe microanalysis study. This was carried out on a Cambridge Instruments Limited 'Geoscan'. The standards used were $CaO.6Al_2O_3$; $CaO.4{\cdot}8Al_2O_3.1{\cdot}2Fe_2O_3$ (20 % substitution of Al by Fe) and $CaO.4Al_2O_3.2Fe_2O_3$ ($33\frac{1}{3}$ % substitution of Al by Fe). Results on the calcium hexaluminate from the used high-alumina brick showed the atomic replacement of Al by Fe to be in the range 12 to 13 %. This is in agreement with results obtained by Hughes (1967, to be published) on used high-alumina bricks from electric arc furnace roofs; using an X-ray diffraction method, he found that up to 21 mol. % of the Al_2O_3 can be replaced by Fe_2O_3. Dayal and Glasser (to be published), basing their work on analyses of fired compacts have shown that a large replacement (up to 40 %) of Al^{3+} by Fe^{3+} can occur in $CaO.6Al_2O_3$ within the system $CaO–Al_2O_3–Fe_2O_3$. Burdese and Brisi (1961) have synthesized the members of the solid solution series $CaO.6(Al, Fe)_2O_3$ and their results are in good agreement with those of Dayal and Glasser.

Investigation of the high-alumina portion of the system $CaO–Al_2O_3$. This involved in the main a study of the melting behaviour of calcium hexaluminate, though the melting point of corundum was also determined. Initially, small (0·6 cm diameter) pellets of pure calcium hexaluminate were pressed from the powder at 5 ton/in^2, after moistening with 5 % starch solution as a binder. The pellets were then fired for 1 hr in argon in a specially constructed vacuum furnace (fig. 6), capable of operating at temperatures in excess of 2000° C, using a tungsten spiral. After quenching, the pellets were examined in polished section and by X-ray diffraction. In the specimens quenched at 1820° and 1860° C, calcium hexaluminate was the only phase present. At 1870° C, α-alumina appeared in trace amount, with glass predominating. In the 1900° (fig. 2), 1925°, and 1950° C quenched microstructures, α-alumina

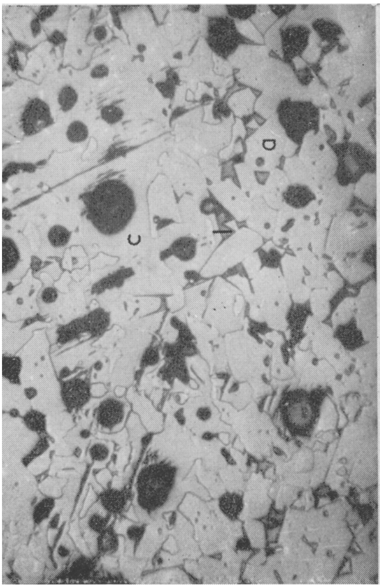

FIG. 1

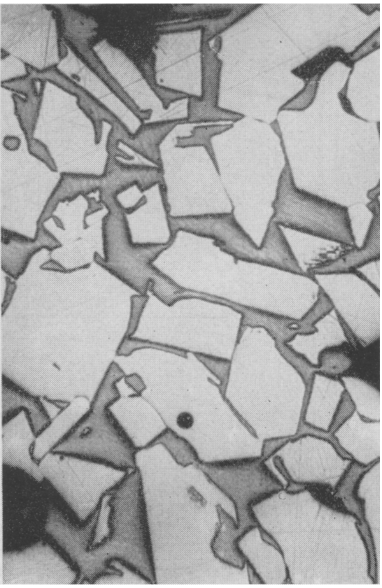

FIG. 2

FIG. 1. Photomicrograph of polished section of body of composition 97 % calcined Al_2O_3, 3 % CaO after firing for 1 hr at 1800° C in argon, then slow-cooled to 1750° C and quenched. Calcium hexaluminate ('c') in large plates, together with equiaxed to tabular grains of alumina ('a'), accompanied by a medium grey glass ('l'). Very dark areas are pores. ×300.

FIG. 2. Photomicrograph of polished section of pellet composed of calcium hexaluminate after firing for 1 hr at 1900° C in argon and quenched. Equiaxial to tabular grains of alumina in a glassy matrix. Very dark areas are pores. ×300.

had increased in amount relative to the glass content. In specimens quenched from the higher temperatures (1970° and 1980° C), alumina dendrites were observed in a glass (fig. 4). These dendrites had crystallized out of the melt on cooling and the material is considered to have been essentially liquid at the firing temperature. The results show the incongruent melting point of calcium hexaluminate to be 1870° C (±10° C), while the liquidus temperature is 1970° C (±10° C); these are in good agreement with results of Auriol *et al.* (1964) and Gentile and Foster (1963). Data obtained during the present investigation are embodied in the phase diagram of the high-alumina portion of the binary system CaO–Al_2O_3 (fig. 3), the melting point of α-alumina having been determined as 2050° C (±10° C).

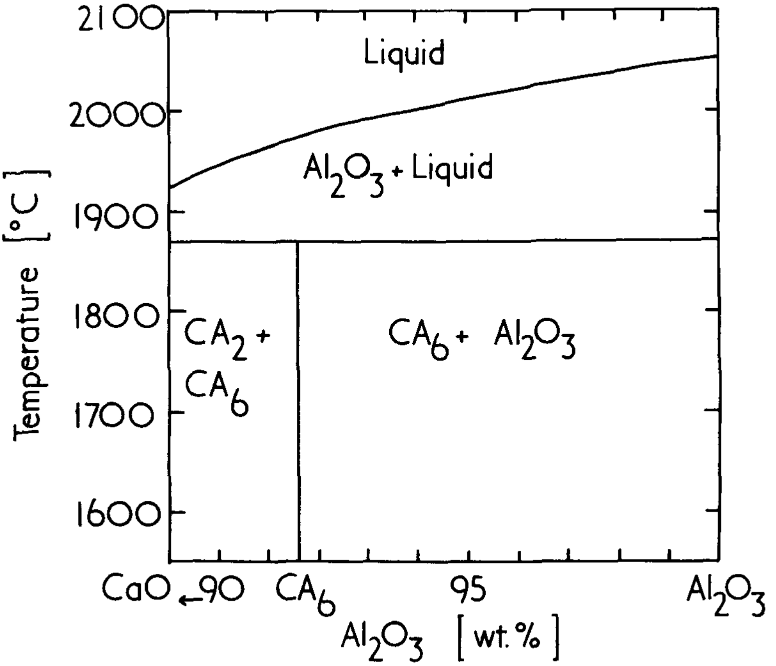

FIG. 3. High alumina portion of CaO–Al_2O_3 system (present investigation).

Occurrence of calcium hexaluminate in used high-alumina refractories from electric arc furnace roofs. Hayhurst and Webster (1964) investigated the microstructure of used 85/86 % alumina bricks taken from electric arc furnace roofs after service at Steel, Peech, and Tozer. These authors identified calcium hexaluminate in a dense 2 to 3 mm-thick zone from the immediate hot face; phase determination was by X-ray diffraction analysis of powdered samples. In their study, extensive use was made of thin, polished-thin and polished sections. In thin section, calcium hexaluminate was bright orange, stated to be due to intake of Fe_2O_3 in solid solution.

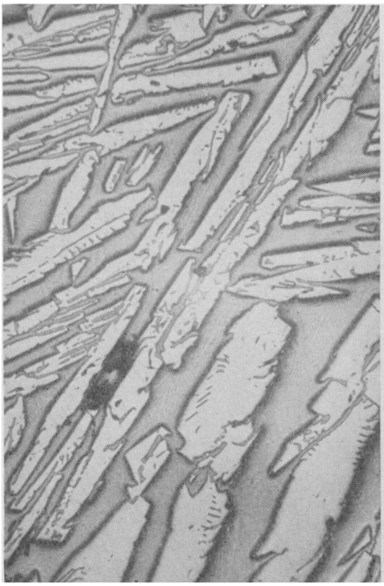

FIG. 4

FIG. 5

FIG. 4. Photomicrograph of polished section of body composed of calcium hexaluminate after firing for 1 h at 1980° C in argon followed by quenching. Dendrites of alumina in a glassy matrix. Infrequent dark areas are pores. × 150.

FIG. 5. Photomicrograph of polished section of immediate hot-face of 84 % alumina brick from fume offtake, electric arc furnace, English Steel Corporation, Tinsley Park, Sheffield. Calcium hexaluminate ('c') has the form of large laths containing relics of alumina ('a') and is associated with hercynite (white) and a dark glass ('l'). Portions of alumina grains broken up by the melt can be observed ('g', on left). Very dark areas are pores. × 300.

The writer first encountered calcium hexaluminate as a major phase in a section cut from immediately behind the hot face of an 84 % alumina brick after service in an electric arc furnace roof (fume-offtakes) at the English Steel Corporation Works at Tinsley Park, Sheffield. The compound has since been observed in a number of used bricks (83–90 %

alumina) from other arc furnace roofs. In polished section (fig. 5), it has the form of light purplish-grey laths of random orientation, in places containing small particles of remnant α-alumina. The aluminate is associated with a spinel, which approximates to hercynite in composition, and with a dark grey glass. The presence of the former two phases together can be explained by the following sequence of reactions, which would be expected to take place when CaO and FeO (both derived from the arc furnace slag) migrate simultaneously into an alumina–mullite composition: mullite would dissociate into anorthite and alumina, while FeO would react with alumina to form hercynite; when mullite is completely decomposed, lime would react with alumina to form calcium hexaluminate, while more FeO would react with alumina to form hercynite. Hayhurst and Webster (1964) have fully discussed the reactions involved and therefore these have only been dealt with briefly in the present account.

The presence of a dense, highly refractory network of calcium hexaluminate crystals at the immediate hot-face of the brick would serve to reduce the incursion of slag solutions into the brick, thus preventing excessive erosion of the latter.

Occurrence of calcium hexaluminate in brick/cement-clinker reaction zone. The compound has been identified by X-ray diffraction during experimental studies of 70 % alumina refractories in contact with cement clinkers at temperatures in the region of 1450° C (Buist and Gelsthorpe, 1967, to be published).

Calcium hexaluminate as a potential industrial material. The compound is currently of interest for microwave applications. Perry (1966) has shown that 1 w/o addition of CaO to a pure alumina, which can lead to the formation of $CaO.6Al_2O_3$ on firing, will cause an increase in the room-temperature microwave permittivity and loss tangent.

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APPENDIX

Details of high-temperature vacuum furnace. This furnace, illustrated diagrammatically in fig. 2, was built specially for the present investigation. It is capable of operating at temperatures in excess of 2000° C, using a tungsten spiral.

The steel furnace body, which was machined out of the solid to reduce leakage, is cylindrical in shape with an outside diameter of 12 in. and is 12 in. in height; the wall thickness is ½ in. The top of the body has a cylindrical water-cooled extension 2 in. in diameter and 2½ in. in height, the upper edge of which is grooved and fitted with an O-ring seal on top of which is a fused quartz window held down by four screws passing into the metal body. The window is used for sighting the optical pyrometer. The base of the furnace body, which is grooved and fitted with an O-ring seal, rests on the water-cooled steel base plate.

The heating spiral is connected to copper electrodes, which enter the furnace through the steel base plate. The spiral itself consists of seven turns (2 mm apart and approximately 16 mm internal diameter) of 2·5 mm tungsten wire bound to the water-cooled copper electrodes with 0·028 in. molybdenum wire. The spiral is enclosed by six concentric radiation shields of thin molybdenum sheet. Five thin molybdenum sheets tied together at the corners by molybdenum wire form the 'lid' or upper radiation shield of the assembly. The upper lead to the spiral passes through a hole in the 'lid' and a second hole, drilled in the 'lid', enables the sighting of the pyrometer on the specimen. The furnace radiation shields are cut away sufficiently at the bottom to permit entry of the lower lead to the spiral. Four thin molybdenum sheets, placed between the base of the spiral and the top of the lower electrode, form the lower radiation shield of the assembly. A small molybdenum cylinder, drilled centrally to minimize conduction loss, was used to support the recrystallized alumina crucible or the box of molybdenum sheet in which the pellet was contained.

The power input to the heating element is controlled by a 100–RM variac operating through a low voltage transformer.

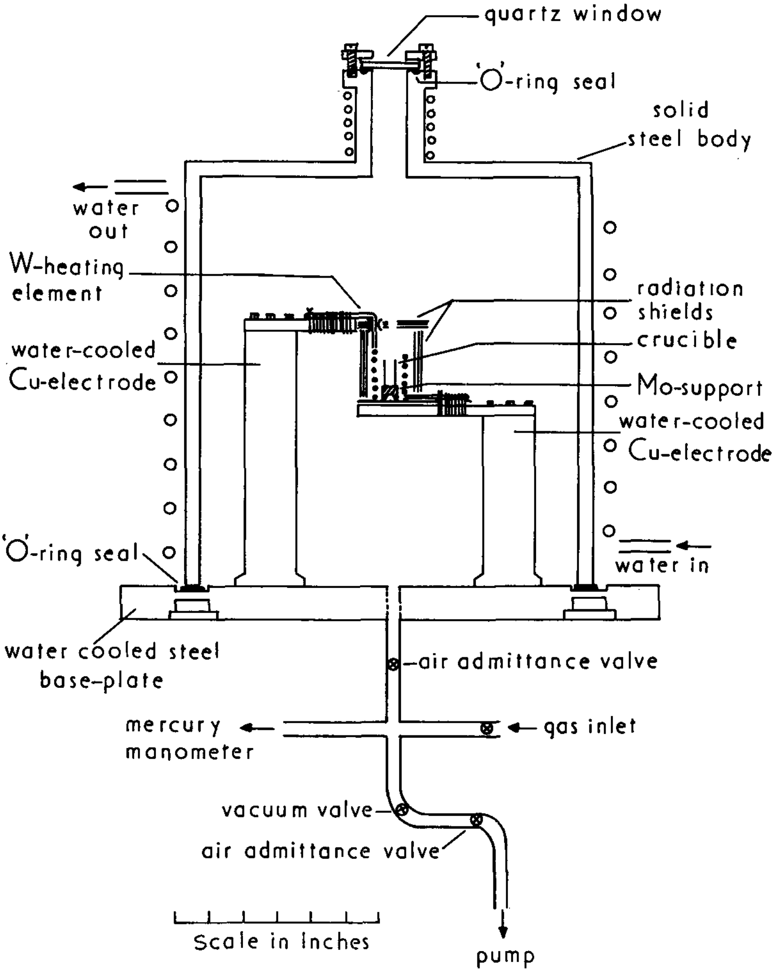

FIG. 6. Diagram of high temperature vacuum furnace.

The vacuum system consists of a Leybold-Elliott two-stage rotary vane pump, which can pump down the system to at least 10^{-3} mm Hg. There is no diffusion pump.

The temperature of the specimen is read by means of an optical pyrometer having a short-focus objective-lens system, mounted on an arm that could be swung over the furnace body; the pyrometer was calibrated by reference to metals of known melting points. During firing, an inert atmosphere of argon at positive pressure is used to suppress volatilization, the gas being introduced into the furnace through a diaphragm and vacuum valves. The argon, supplied by Saturn Industrial Gases, Limited, has a purity of 99·99 %. A mercury manometer is also included in the system. This can be used to indicate the rate of change of pressure when the gas is being introduced into the furnace and also, during firing, provides an outlet for the gas. With this furnace, removal of the specimens at temperature is not possible, but this is not a serious disadvantage, since a very rapid cooling rate can be achieved by switching off the current.