# The occurrence of artificial kalsilite and allied potassium aluminium silicates in blast-furnace linings.

(With Plate IV.)

By G. R. RIGBY, Ph.D.

and H. M. RICHARDSON, B.Sc.

British Refractories Research Association, Stoke-on-Trent.

———

## I. INTRODUCTION.

THE contour and dimensions of a typical blast furnace are shown in fig. 1. The shell of the furnace consists of riveted steel plates, inside which is a lining of firebricks varying in thickness about 2–3½ feet. Molten iron collects in the crucible or hearth at the bottom of the furnace and is periodically run off through a hole in the side of the furnace known as the tap-hole. The hearth is lined with firebrick both around the sides and along the floor, the total thickness of brickwork below the hearth in fig. 1 being 3 feet 9 inches.

A blast furnace after completely relining with firebrick may be in continuous operation for several years during which period upwards of a million tons of iron may be made, necessitating the charging of some 2–3 million tons of iron ore, coke, and limestone through the bell at the top of the furnace. When the furnace is in blast the firebrick lining is exposed to the abrading action of the descending burden and the cutting effect of the ascending blast charged with fine particles of coke and ore. The brickwork is also chemically corroded, being exposed to alkali vapours, lime-bearing slags, and the disintegrating action of carbon monoxide which dissociates, depositing carbon within the brick structure.

It has long been the practice of the British Refractories Research Association to examine blown-out furnace linings with a view to determining which zones in the furnace are subjected to the most severe wear. Samples of the slagged brickwork are also removed for laboratory examination.

A common feature of the brickwork in the middle and lower stack region is that the hot face of the lining is often vitrified due to alkali

vapours reacting with the alumina and silica in the brickwork, forming alkali alumino-silicates. A typical thin section cut inwards from the working face often reveals crystals of orthorhombic $KAlSiO_4$, while farther towards the brick mullite and leucite can be detected. More
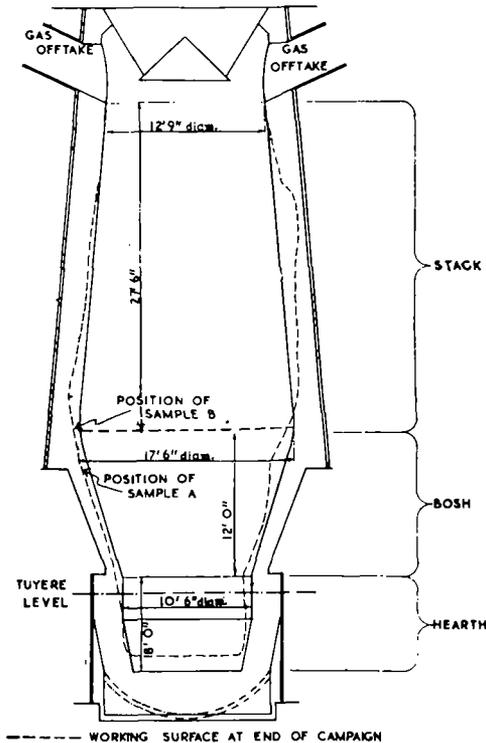


FIG. 1. Section of Kettering no. 3 blast furnace, showing extent of wear of firebrick lining and position of specimens A and B.

recently various samples have been subjected to X-ray examination by the Debye-Scherrer powder method when the presence of kalsilite has been confirmed by comparing the results with the X-ray powder data given by F. A. Bannister.[1] A. H. Jay (see Appendix) of the United Steel Companies has also independently verified the presence of kalsilite in samples taken from blast-furnace stacks. These minerals, kalsilite, orthorhombic $KAlSiO_4$, and leucite, would appear to be readily formed

[1] F. A. Bannister and M. H. Hey, Min. Mag., 1942, vol. 26, p. 218.

by the action of alkali vapours on firebricks under the conditions pre-
vailing in the blast furnace, but until quite recently they have only been
detected associated with glass or admixed with furnace burden adhering
to the surface of the brickwork and they could not be obtained in any-
thing approaching a state of purity.

## II. THE HEARTH OF THE KETTERING NO. 3 FURNACE.

A few months ago an opportunity was given to one of the authors by
the Kettering Iron and Coal Co. to examine their no. 3 furnace. This



Iron bear w'th TiCN.
Vitrified brick 2" thick (grey).
Black glassy layer of brickwork.
Grey powdery brick with holes.
White powdery layer, pink at top, Kalsilite.

Original surface of brickwork ——————
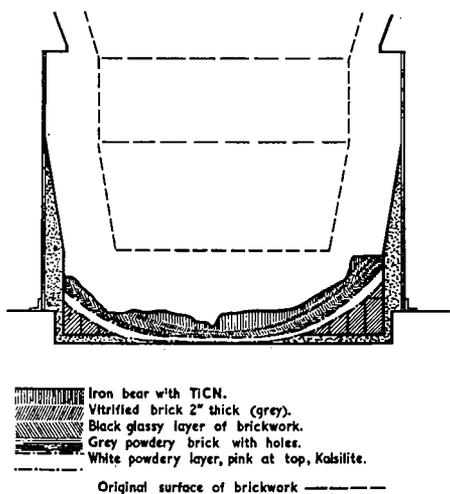
FIG. 2. Section of hearth of blast furnace, showing zoning of deposits.

furnace, the dimensions of which are given in fig. 1, had been in blast
for six years and had made some 250,000 tons of iron. The stack of the
furnace had been lined with bricks of the following percentage composi-
tion: $SiO_2$ 55·6, $Al_2O_3$ 40·3, $Fe_2O_3$ 0·84, MgO 0·27, CaO 0·28, $Na_2O$ 0·37,
$K_2O$ 2·02, while the percentage analysis of the bosh and hearth brick-
work was as follows: $SiO_2$ 53·5, $Al_2O_3$ 42·4, $Fe_2O_3$ 2·6, MgO 0·5, CaO 0·4,
$Na_2O$ trace, $K_2O$ 0·1. The contours of the brickwork before and after the
furnace campaign are shown in fig. 1. Samples of brickwork were taken
at intervals all down the stack, and vitrification of the working face of
the lining consequent upon alkali attack was a noticeable feature of some
of these samples. Before excavating the hearth it was first necessary to
remove a quantity of frozen iron which had collected due to the floor of

the hearth having been eroded to a dish-shaped contour extending below
the tap-hole level. The next procedure was to remove the brickwork
remaining below this mass of frozen iron. Under the combined influences
of pressure, temperature, and reducing conditions it is common to find
that this brickwork has vitrified to a porcelain-like monolithic mass, but
with the furnace in question a most unusual condition was observed.
A vertical section cut through the hearth showed the presence of a
number of well-defined zones which are depicted in fig. 2. The upper-
most zone extending to a depth of 2 inches consisted of vitrified brick-
work; this was followed by a second zone having a black glassy appear-
ance, also extending for a depth of 2 inches. This zone was found to
consist of glass containing numerous cordierite crystals. The zone below
this was some 5 inches deep and consisted of a white, soft, powdery
material with a strong smell of cyanide. The upper portion of this zone
was coloured pink and at the centre of the hearth the white material
had displaced the layer of coke and tar ramming on which the hearth
brickwork was built. Below this white zone near to the wall of the hearth
the original brickwork could be identified, the bricks were intensely
vitrified but the joints between individual bricks were clearly defined.
The curved nature of these zones and their sharp demarcation were, no
doubt, imposed by the temperature gradients in the hearth, the iso-
therms following a similar curvature.

### III. Examination of the White Deposit.

The material was found to consist largely of kalsilite, the chief
impurity being potassium carbonate. In spite of the strong smell of
cyanide pervading the samples, analysis showed that the actual cyanide
content was below 0·25 %. This was, however, sufficient to give colour
reactions with the iron oxide, and the grey-white material gave an
intense green coloration on adding hydrochloric acid. Various samples
were taken across the hearth; sample I gave the following percentage
analysis: $SiO_2$ 32·1, $TiO_2$ 0·70, $Al_2O_3$ 29·1, $Fe_2O_3$ 1·5, $MgO$ 0·27, $CaO$ 0·50,
$Na_2O$ 2·2, $K_2O$ 29·1, loss on ignition 4·2 ($CO_2$ 3·5), cyanides trace. The
percentage analysis of a second sample was: $SiO_2$ 30·0, $TiO_2$ 0·35, $Al_2O_3$
26·4, $Fe_2O_3$ 1·4, $MgO$ 0·12, $CaO$ 0·45, $Na_2O$ 2·7, $K_2O$ 30·3, loss on ignition
7·2 ($CO_2$ 6·3). These analyses indicate that sample I consisted of about
90 % kalsilite, 5·7 % potassium carbonate, and 4·3 % excess alumina,
ferric oxide, lime, and magnesia. Similar figures for sample II are:
81 % kalsilite, 12·2 % potassium carbonate, and 6·8 % excess silica,
alumina, ferric oxide, &c.

Specific gravity determinations were made on a number of samples which were first purified from potassium carbonate by floatation in a benzene-bromoform solution of density 2·4. The heavier material had densities ranging from 2·60 to 2·61. A thin section was cut from a piece of lumpy material from sample I. The crystals were very small, the largest being only about 0·07 mm. long. Under a 2-mm. oil-immersion objective good almost uniaxial negative interference-figures were obtained from several crystals. Refractive indices obtained by the Becke method were $\omega$ 1·537, $\epsilon$ 1·530 ($\pm$0·002). None of the crystals possessed a hexagonal outline: the majority were rectangular in shape as may be seen from pl. IV, fig. 3. The crystals were elongated parallel to the slow direction (i.e. had positive elongation), indicating a tabular habit. No suggestion of any cleavages was apparent in any of the crystals.

X-ray powder photographs of the two samples were also taken using a 9-cm. camera and filtered cobalt radiation (pl. IV, figs. 8 and 9). The lattice spacings recorded in table I agree remarkably well with those previously recorded by F. A. Bannister for the natural mineral kalsilite found in rocks from Mafuru, Uganda. Observed and calculated values for $\sin^2\theta$, where $\theta$ is the Bragg angle, are also listed in table I, the calculated values being obtained from the lattice dimensions of natural kalsilite as given by F. A. Bannister, viz.: $a$ 5·17, $c$ 8·67 kX. The relative intensities of the reflections given by samples I and II are also listed and it will be observed that there are differences in the intensities of certain of the reflections. X-ray examination of samples containing kalsilite previously found in the stacks of two blast furnaces at two other plants gave photographs in which the relative intensities as well as the positions of the reflections agreed with those of sample I rather than sample II. It should be emphasized that these intensity differences are not accompanied by any noticeable line movement indicative of solid solution effects, but it would appear that differences occur in the reflecting power of the atom-bearing planes in the various samples. Differences in chemical analysis between samples I and II do not appear to account satisfactorily for these intensity variations, as, for example, the higher percentage of potassium carbonate in sample II. It will also be observed that the percentages of ferric oxide, lime, and soda are of a similar order in the two samples. The intensity values reported for natural kalsilite generally agree with those obtained for sample I rather than for sample II.

TABLE I. X-ray data for kalsilite. For the natural mineral from F. A. Bannister, 1942. Bravais indices omitting the third index.

| Relative intensities. | | $d$ (kX) Artificial | $d$ (kX) Natural | | Sin²$\theta$ Artificial | Sin²$\theta$ Calculated for |
|---|---|---|---|---|---|---|
| Sample I. | Sample II. | mineral. | mineral. | $hkl$. | mineral. | natural mineral. |
| m | vw | 4·33 | 4·35 | 002 | 0·0426 | 0·0425 |
| s | s | 3·96 | 3·97 | 101 | 0·0511 | 0·0505 |
| vs | s | 3·10 | 3·11 | 102 | 0·0832 | 0·0824 |
| s | vs | 2·569 | 2·590 | 110 | 0·1212 | 0·1195 |
| m | m | 2·454 | 2·470 | 111 | 0·1326 | 0·1302 |
| m | vw | 2·415 | 2·428 | 103 | 0·1369 | 0·1355 |
| m | m | 2·208 | 2·218 | 112 | 0·1638 | 0·1602 |
| s | m | 2·161 | 2·163 | 004 | 0·1711 | 0·1701 |
| w | w | 1·979 | 1·984 | 202 | 0·2040 | 0·2019 |
| vw | vw | 1·948 | 1·955 | 104 | 0·2104 | 0·2099 |
| w | w | 1·921 | 1·926 | 113 | 0·2167 | 0·2152 |
| w | w | 1·764 | 1·770 | 203 | 0·2566 | 0·2550 |
| m | m | 1·654 | 1·660 | 114 or 211 | 0·2921 | 0·2895, 0·2896 |
| m | w | 1·615 | 1·620 | 105 | 0·3062 | 0·3056 |
| s | m | 1·570 | 1·576 | 212 | 0·3239 | 0·3214 |
| m | vw | 1·552 | 1·556 | 204 | 0·3314 | 0·3294 |
| s | s | 1·485 | 1·490 | 300 | 0·3624 | 0·3586 |
| m | w | 1·456 | 1·460 | 213 | 0·3770 | 0·3746 |
| vw | vw | 1·443 | n.d. | 006 | 0·3838 | 0·3827 |
| m | w | 1·369 | 1·375 | 106 | 0·4261 | 0·4225 |
| w | w | 1·330 | 1·335 | 214 | 0·4512 | 0·4490 |
| m | m | 1·286 | 1·294 | 220 | 0·4826 | 0·4781 |
| m | w | 1·261 | 1·264 | 116 | 0·5022 | 0·5022 |
| m | w | 1·226 | 1·231 | 311 or 304 | 0·5317 | 0·5286 |
| m | w | 1·209 | 1·212 | 215 | 0·5462 | 0·5446 |
| m | m | 1·189 | 1·194 | 312 | 0·5651 | 0·5604 |
| w | w | 1·138 | 1·141 | 313 | 0·6169 | 0·6136 |
| vw | vw | 1·108 | 1·111 | 401 or 221 | 0·6512 | 0·6481, 0·6482 |
| w | w | 1·081 | 1·085 | 402, 207, or 008 | 0·6836 | 0·6801, 0·6802, 0·6803 |
| w | vw | 1·054 | 1·055 | 108 | 0·7181 | 0·7201 |
| w | vw | 1·038 | 1·036 | 225 | 0·7419 | 0·7437 |
| m | w | 1·007 | 1·011 | 315 | 0·7854 | 0·7837 |
| vw | vw | 1·000 | 1·000 | 322 or 118 | 0·7991 | 0·7991, 0·7998 |

## IV. THE OCCURRENCE OF POTASSIUM-ALUMINIUM SILICATES IN BLAST-FURNACE SAMPLES.

N. L. Bowen[1] recognizes two distinct crystal phases of $KAlSiO_4$. The low-temperature phase is hexagonal, isomorphous with nepheline, uniaxial negative, with $\omega$ 1·532, $\epsilon$ 1·527. Natural kaliophilite from Monte Somma may be identical with this low-temperature phase, and S. J. Thugutt[2] claims to have prepared artificial kaliophilite at 208–211° C. identical with the natural mineral. N. L. Bowen also recognizes a high-

---

[1] N. L. Bowen, Amer. Journ. Sci., 1917, ser. 4, vol. 43, p. 115. [M.A. 1–167.]

[2] S. J. Thugutt, Arch. Min. Tow. Nauk. Warszaw., 1937, vol. 13, p. 112. [M.A. 7·146.]

temperature form of kaliophilite which is orthorhombic, optically negative, and twins similar to aragonite, with $\alpha$ 1·528, $\gamma$ 1·536. More recently, M. H. Hey (Bannister and Hey, loc. cit., 1942) has succeeded in preparing an orthorhombic form of $KAlSiO_4$ twinned like aragonite. Bowen states that both the hexagonal and orthorhombic forms of $KAlSiO_4$ can be obtained at low temperatures, but the hexagonal form inverts to the orthorhombic form in the neighbourhood of 1540° C.

Good crystals of orthorhombic $KAlSiO_4$ can often be observed in the slagged face of brick samples from blast furnaces. Pl. IV, fig. 4, is a thin section cut from slagged brickwork from the stack at position A (text-fig. 1) (sample A). The X-ray pattern showed the presence of $KAlSiO_4$ free from leucite (fig. 11). The crystals were not entirely homogeneous, a few were uniaxial negative, basal sections were hexagons while other sections were square or rectangular in outline. Other crystals appeared to be biaxial positive with a very small axial angle. These crystals showed interpenetration twinning of the aragonite type. The refractive indices were $\alpha$ 1·534, $\gamma$ 1·540. In contrast with kalsilite the rectangular sections had negative elongation, there was also a suggestion of a cleavage parallel to $c$.

A sample obtained from the stack of the Kettering furnace at position B (fig. 1) had a vitrified working face and a thin section revealed well-developed crystals (fig. 5). Some of these crystals showed complex polysynthetic twinning sometimes in more than one direction. They were biaxial positive with refractive indices $\alpha$ 1·528, $\gamma$ 1·533. The crystals tended to a prismatic or lath form, the laths having negative elongation. Away from the edge of the section the crystals progressively altered, the twinning became less pronounced and finally disappeared, while the birefringence increased until crystals similar to those shown in fig. 4 were encountered. Crystals similar to these have been noticed previously and an illustration is given in fig. 6 where they occurred in a sample obtained from a blast-furnace stove. X-ray photographs of sample B showed the presence both of orthorhombic $KAlSiO_4$ and leucite (fig. 12).

With regard to the number of crystalline forms of $KAlSiO_4$ and their relative stability the following observations can be made from a study of blast-furnace samples.

(1) Optically uniaxial negative crystals of orthorhombic $KAlSiO_4$ free from twinning have been observed in samples which have been exposed for long periods at temperatures around 1000–1100° C. X-ray powder

photographs have shown that these crystals are orthorhombic (pseudo-hexagonal).

(2) Optically biaxial positive crystals twinned like aragonite have also been observed, and in addition biaxial positive crystals with complicated twinning like leucite have been noticed and these crystals have been associated with leucite. Such crystals have been formed in close proximity to the uniaxial negative form of orthorhombic $KAlSiO_4$ and give the same X-ray photograph.

(3) A massive deposit of kalsilite contaminated with 5–10 % of potassium carbonate has been found in the blast-furnace hearth some 4 or 5 inches below molten iron. The temperature of formation of this kalsilite must therefore be in the region 700–1100° C.

(4) Kalsilite has been detected in stack samples from blast furnaces where the temperature range would again be 700–1100° C.

It is not the purpose of this paper to explain how the deposit of kalsilite originated below the hearth, but it is of some importance with regard to the stability of the $KAlSiO_4$ minerals to suggest the mechanism of their synthesis in the furnace. It has long been appreciated that alkalis are present in the blast furnace, and the flue dust passing over with the gases has sometimes been treated for the recovery of alkalis. The alkali content of the ore supplying the Kettering furnace is not known, but assuming it to be as low as 0·1 % this represents the intro-duction of no less than 750 tons of alkali into the furnace during its six years' campaign. It is probable that the potash continuously accumu-lates inside the furnace, being vaporized at the tuyere level and con-densing again when it meets the cooler materials at the top of the furnace. The management have occasionally noticed the presence of molten potassium cyanide floating on the iron as it is tapped from the furnace. It is probable that the alkali is initially vaporized as cyanide or chloride, but at certain positions in the furnace these salts are decom-posed by free iron oxide or water vapour to the corresponding oxides which then slag the brickwork. The potassium carbonate found with the kalsilite probably originated from the hydrolysis of the cyanide since the hearth was finally cooled by means of water-sprays after all possible iron had been tapped from the furnace. The alumina and silica must have been derived from the fire-bricks and it is interesting in this con-nexion to observe that the molecular ratio of alumina to silica is almost 1:2. This being the case it should be possible to synthesize kalsilite in the laboratory without resorting to hydrothermal methods at high pressures since the pressure in the blast furnace is only a few centimetres

of mercury higher than atmospheric. Accordingly, a number of experiments were conducted in the laboratory to try and establish the relationship between kalsilite and kaliophilite.

## V. THE SYNTHESIS OF POTASSIUM ALUMINIUM SILICATES IN THE LABORATORY.

(a) *The synthesis of kaliophilite.*—The experiments were mainly carried out with the object of synthesizing kalsilite. A china-clay was chosen as a source of silica and alumina in which the molecular proportion of these constituents was 2:1 and other impurities were low. The percentage analysis of the china-clay was as follows: $SiO_2$ 46·90, $Al_2O_3$ 39·08, $Fe_2O_3$ 0·66, MgO 0·02, CaO 0·05, $Na_2O$ 0·14, $K_2O$ 0·42, loss on ignition 12·72. Four mixtures were made up of the following compositions:

(1) One molecular proportion of china-clay and one molecular proportion of potassium carbonate.

(2) As no. (1) with the addition of 5 % of $Fe_2O_3$.

(3) As no. (1) with the addition of 5 % of kalsilite.

(4) As no. (1) but with twice the amount of potassium carbonate.

The materials were placed in a furnace and heated for various periods at temperatures of 900° C. (60 hours), 1100° C. (5 hours), and 1300° C. (5 hours). A stream of nitrogen saturated with water vapour at 25° C. was maintained through the furnace. X-ray photographs of the materials gave the following information. When heated to 900° C. all specimens gave the same X-ray pattern (pl. IV, fig. 7). This pattern was distinct from that given by the kalsilite or orthorhombic $KAlSiO_4$ from sample A in the blast furnace. Examination of the X-ray photographs suggests that this low-temperature form of $KAlSiO_4$ is hexagonal and it is probably identical with the low-temperature form previously described by N. L. Bowen. It can be indexed according to the data for natural kaliophilite given by F. A. Bannister, $a$ 27, $c$ 8·51 kX.

When heated to 1100° C. nos. (1) and (3) specimens still gave the same pattern as at 900° C., no. (2) specimen gave mainly the same pattern as at 900° C. but there was a pattern developing identical with that obtained from the blast-furnace sample A. Specimen (4) gave a pattern which was identical with that obtained from sample A (fig. 11). This is probably the high-temperature orthorhombic form of $KAlSiO_4$ described by N. L. Bowen. This form of $KAlSiO_4$ appears to be the stable modification at high temperatures, the inversion temperature being between

900 and 1100° C. When heated to 1300° C. all specimens gave patterns similar to that of sample A, but in specimens nos. (1) and (3) additional lines corresponding to leucite could be detected, suggesting that alkali was being volatilized from these two specimens.

F. A. Bannister has kindly supplied a sample of an orthorhombic form of $KAlSiO_4$ showing twinning of the aragonite type, and X-ray examination showed this to be identical with blast-furnace sample A and the high-temperature orthorhombic form prepared by us. The optical properties of this orthorhombic form appear, however, to vary in certain samples, e.g. in sample A the crystals appear to be pseudo-hexagonal and twinning is not marked. Other samples show twinning of the aragonite type, and finally there are well-developed crystals as in sample B with polysynthetic twinning similiar to microcline or leucite. These latter samples appear to have a lower birefringence, lower refractive indices, and a larger axial angle than the untwinned types. There would appear to be some disagreement with regard to the optical sign of the orthorhombic form, which we find to be biaxial positive in the crystals exhibiting complicated twinning (pl. IV, figs. 5 and 6). These variations might be accounted for by partial loss of potash due to volatilization; it appears significant that orthorhombic $KAlSiO_4$ showing polysynthetic twinning is associated with leucite.

The lattice spacings for the low-temperature and orthorhombic forms of $KAlSiO_4$ are given in table II and the X-ray photographs in figs. 7 and 11.

(b) *The synthesis of kalsilite.*—Since kalsilite was obtained in none of the above experiments, small specimens of kalsilite from the furnace hearth contaminated with the potassium carbonate associated with this deposit were heated at 900°, 1100°, and 1300° C. respectively. X-ray examination showed that the specimen was unchanged after heating to 900° and 1100° C., but the specimen fired to 1300° C. had begun to decompose to orthorhombic $KAlSiO_4$, giving an additional X-ray pattern identical with that obtained from blast-furnace sample A. This alteration at 1300° C. requires time to complete and intermediate specimens were obtained showing the kalsilite pattern together with a pattern similar to that obtained on heating the china-clay and potassium carbonate mixes to 900° C., indicating that with this deposit the alteration from kalsilite to orthorhombic $KAlSiO_4$ was by way of this low-temperature hexagonal form. These experiments suggested that the upper temperature limit for synthesizing kalsilite would be below 1300° C.

TABLE II. Main space-lattice reflections of the high-temperature orthorhombic KAlSiO$_4$ (fig. 11) and of the low-temperature hexagonal form, kaliophilite (fig. 7).

| High-temperature ortho-rhombic form. | | Low-temperature hexagonal form, kaliophilite. | |
|---|---|---|---|
| Intensity. | d (kX). | Intensity. | d (kX). |
| w | 6·21 | w | 4·50 |
| m | 5·75 | m | 4·26 |
| w | 4·51 | s | 3·10 |
| m | 4·26 | fs | 2·61 |
| w | 3·88 | m | 2·22 |
| fs | 3·56 | m | 2·14 |
| m | 3·41 | vw | 1·65 |
| w | 3·30 | w | 1·58 |
| s | 3·10 | vw | 1·55 |
| fs | 2·79 | w | 1·50 |
| m | 2·67 | w* | 1·25 |
| fs | 2·61 | vw* | 1·19 |
| m | 2·23 | | |
| m | 2·13 | | |
| vw | 2·10 | | |
| w | 2·07 | | |
| w | 1·76 | | |
| m | 1·72 | | |
| w | 1·58 | | |
| m | 1·48 | | |
| w | 1·425 | | |
| m | 1·25 | | |
| w | 1·23 | | |
| m | 1·20 | | |

* Diffuse lines on the photograph.

Since small additions of ferric oxide had failed to produce kalsilite when added to the appropriate china-clay and potassium carbonate mixes, additions of lime as calcium carbonate, metallic iron, and alumina were next tried, but without success. The chemical analyses of kalsilite both from natural sources and from the blast-furnace hearth showed the presence also of soda and magnesia; accordingly experiments were made with an addition of sodium carbonate equivalent to 3 % of Na$_2$O. On heating this mixture to 850° C. in a furnace through which a stream of nitrogen saturated with water vapour was passed a specimen was obtained which gave a good X-ray photograph of kalsilite free from kaliophilite or unreacted materials (pl. IV, fig. 10). Further experiments elucidated that an atmosphere saturated at 25° C. with water vapour was not necessary. Rather surprisingly, if the china-clay was substituted by powdered firebrick similar to that used in the hearth of the blast furnace the reaction proceeded more readily and at 850° C. the mixture was converted to kalsilite in a few hours.

F

A series of experiments was finally carried out to determine more closely the stability range of this mineral. The following mixes were made up for these experiments:

(1) Powdered firebrick (analysis given earlier in the paper) with the addition of the appropriate amount of potassium carbonate plus 0·5 % $Na_2O$ (as carbonate) based as a weight percentage on the composition $KAlSiO_4$.

(2) Similar to mix (1) with the addition of sodium carbonate equivalent to 1·0 % $Na_2O$.

(3) Similar to mix (1) with the addition of 1·5 % $Na_2O$.

(4) As mix (1) with the addition of 2·0 % $Na_2O$.

(5) As mix (1) with the addition of 5·0 % $Na_2O$.

(6) A mix consisting of equimolecular proportions of the two carbonates to give the theoretical composition $(Na,K)AlSiO_4$.

These mixes were then heated at temperatures of 650°, 750°, 850°, 1000°, 1100°, and 1200° C. At 650° C. the reaction was slow and unchanged brick was still present at the end of 5 hours. At all other temperatures kalsilite was obtained with the specimens containing additions of 2 % and 5 % soda, but increase in soda content caused line movement in the kalsilite pattern. At temperatures of 650°, 750°, and 850° C. the specimens containing 0·5, 1·0, and 1·5 % additions of soda gave the low-temperature hexagonal kaliophilite, while at 1000°, 1100°, and 1200° C. the specimens containing 0·5 and 1·0 % additions gave the high-temperature orthorhombic $KAlSiO_4$. At 1100° and 1200° C. mix (3) containing 1·5 % addition of soda gave a photograph indicating a mixture of kalsilite and orthorhombic $KAlSiO_4$. Mix (6) containing equimolecular proportions of sodium and potassium gave two solid phases; variations in the space-lattice indicated that these were a sodium-rich kalsilite together with a potassium-rich nepheline. It would appear therefore that a small percentage of sodium is essential for kalsilite to crystallize out, the minimum amount being equivalent to more than 1·5 % and less than 2·0 % $Na_2O$ based on the theoretical amount of kalsilite which can be formed. In this connexion it is interesting to note that the analysis of natural kalsilite given by M. H. Hey contained 2 % of $Na_2O$ if the impurities are ignored, while the kalsilite from the blast-furnace hearth was associated with 2·5–3·0 % of $Na_2O$. It is also probable that this minimum amount of sodium varies with the temperature of formation.

The decomposition at 1300° C. of a specimen prepared from the

kalsilite deposit found in the blast furnace suggests that kalsilite becomes unstable at some temperature below its melting-point. Experiments undertaken to determine the range of stability showed that kalsilite containing 1·5 % of soda was decomposed at 1300° C.; with 2·0 % of soda the temperature of decomposition was between 1300° and 1350° C.; and with 5 % soda kalsilite was stable at 1500° C. From changes in the space-lattice as revealed by X-ray photographs, the limit of replacement of potassium by sodium at 1100° C. is reached with the addition of 5 % $Na_2O$. Although changes in lattice spacings were noted with kalsilite containing varying amounts of sodium no difference in relative intensities comparable with those given by the blast-furnace samples were observed.

## VI. GENERAL CONCLUSIONS.

Our experiments and observations would indicate the existence of three minerals having the chemical composition $KAlSiO_4$.

The low-temperature modification is hexagonal and is probably similar to natural kaliophilite. It is formed when the correct proportions of silica, alumina, and potash are heated below 900° C.

The high-temperature modification is orthorhombic and is synthesized by heating the correct proportions of silica, alumina, and potash at temperatures over 1000° C. This orthorhombic form of $KAlSiO_4$ has been found in blast-furnace linings. Occasionally crystals are almost uniaxial and free from twinning, other crystals are biaxial positive and exhibit twinning like aragonite, while still other crystals are biaxial positive and show polysynthetic twinning sometimes in two directions. It is suggested that these differences are due to some loss of potash by volatilization, as the form showing polysynthetic twinning is usually associated with leucite.

The third mineral, kalsilite, can only be formed in the presence of sodium. With 1·5 % addition of $Na_2O$ to the correct mixture of silica, alumina, and potash, some kalsilite is formed at 1100° and 1200° C. With 2 % and 5 % $Na_2O$ additions kalsilite is readily formed on heating to temperatures above 650° C. The upper temperature limit of stability is also dependent on the sodium content; with 1·5 % $Na_2O$, kalsilite is decomposed to orthorhombic $KAlSiO_4$ below 1300° C., with 2 % of $Na_2O$ the temperature of decomposition is between 1300° and 1350° C., and with 5 % of $Na_2O$ it is above 1500° C.

to examine their blast furnace and collect samples; Dr. F. A. Bannister of the British Museum for the interest he has shown in the research; Mr. A. T. Green, Director of the British Refractories Research Association for permission to publish this paper, Miss F. Ball for her assistance in the laboratory, and Mr. W. Hugill for taking the photographs.

----

### Explanation of Plate IV.

Artificial potassium aluminium silicates. Figs. 3–6, photomicrographs of thin sections. Figs. 7–12, X-ray powder photographs taken in a 9-cm. camera with filtered cobalt radiation, 1·787 kX.

Fig. 3. Artificial kalsilite excavated from below the hearth (text-fig. 2), sample 1. × 200.

Fig. 4. Thin section cut from the slagged brickwork in the stack (position A, text-fig. 1), sample A, showing crystals of orthorhombic $KAlSiO_4$. × 100.

Fig. 5. Thin section from vitrified working face of the stack (position B, text-fig. 1), sample B, showing orthorhombic $KAlSiO_4$ and leucite. × 100.

Fig. 6. Orthorhombic $KAlSiO_4$, showing polysynthetic twinning, from a blast-furnace stove.

Fig. 7. Artificial kaliophilite prepared in the laboratory, p. 83.

Fig. 8. Artificial kalsilite, sample 1 (fig. 3), excavated from the hearth of the Kettering no. 3 furnace; chemical analysis, p. 78, X-ray data, p. 80.

Fig. 9. Artificial kalsilite, sample 2, excavated from hearth of Kettering no. 3 furnace; chemical analysis, p. 78; X-ray data, p. 80.

Fig. 10. Artificial kalsilite prepared in the laboratory, p. 85.

Fig. 11. Orthorhombic $KAlSiO_4$, sample A, from the stack at position A (cf. figs. 1 and 4).

Fig. 12. Orthorhombic $KAlSiO_4$ and leucite, sample B, from the stack at position B (cf. figs. 1 and 5).

----

### Appendix.

*X-ray reflections of kalsilite $(K_2O.Al_2O_3.2SiO_2)$.*

By A. H. JAY,[1] Ph.D., F.Inst.P and K. W. ANDREWS, D.Phil.

The United Steel Companies Limited, Research and Development Department, Stocksbridge, near Sheffield.

Our first experience of this mineral and the other potassium aluminium silicates, kaliophilite, and leucite was during an examination of samples taken from a scaffold which was removed from no. 1 blast furnace at Appleby-Frodingham in August 1945. The minerals were identified by

----

[1] Alfred Hartley Jay (1906-47) had been working on this same problem and this appendix contains his notes dated February 19, 1947. He died on February 26, 1947, after a motor-car accident on February 22. Two papers by him in this Magazine (1944, vol. 27, pp. 54 and 56) gave much promise of further useful work.

means of X-ray data given in the X-ray card index (data by Bannister). In this scaffold the minerals kalsilite and kaliophilite were present in zones, but the reason for their localized appearance was not apparent. Thin layers of almost pure kalsilite were found in samples of slagged fireclay bricks which had been removed from the stacks of other blast furnaces at Appleby-Frodingham and at the Kettering Iron and Coal Co., Ltd. This note records accurate line spacings and chemical analysis of a well-crystalline and reasonably pure sample, and provides confirmation of Bannister's data, minor changes being due to the effects of different chemical composition. Chemical analysis of the kalsilite gave:

| SiO$_2$. | Al$_2$O$_3$. | FeO. | MgO. | Na$_2$O. | K$_2$O. | H$_2$O($<300°$ C.) | C. | traces. |
|---|---|---|---|---|---|---|---|---|
| 36·0 | 29·8 | 0·35 | 0·2 | [n.d.] | 27·0 | 0·5 | 4·0 | $<0·1\%$ |
| 0·599 | 0·292 | 0·005 | 0·005 | — | 0·287 | molecular ratios. | | |

X-ray powder data for kalsilite calculated from $a$ 5·150$_5$, $c$ 8·684$_5$kX ($c/a$ 1·686), with observed intensities. Bravais indices omitting the third index.

| hkl. | Intensity. | d (kX). | hkl. | Intensity. | d (kX). |
|---|---|---|---|---|---|
| 002 | wm | 4·342 | 215 | m | 1·2097 |
| 101 | m | 3·968 | 312 | m | 1·1898 |
| 102 | s | 3·112 | 313 | wm | 1·1376 |
| 110 | ms | 2·575 | 224 | w | 1·1075 |
| 111 | wm | 2·469 | 401 | vw | 1·1061 |
| 103 | w | 2·428 | 402 | wm | 1·0800 |
| 200 | vw | 2·230 | 108 | wm | 1·0548 |
| 112 | w | 2·215 | 403 | vw | 1·0406 |
| 004 | m | 2·171 | 306 | w | 1·0371 |
| 201 | w | 2·160 | 321 | vvw | 1·0163 |
| 202 | w | 1·984 | 315 | m | 1·0077 |
| 104 | vw | 1·952 | 217 | vw | 0·9992 |
| 113 | w | 1·924 | 322 | vw | 0·9961 |
| 203 | w | 1·767 | 208 | wm | 0·9761 |
| 114 } 211 } | wm | 1·660 1·655 | 410 | wm | 0·9733 |
| 105 | m | 1·618$_5$ | 009 } 323 } | w | 0·9650 0·9648 |
| 212 | m | 1·571$_5$ | 226 | m | 0·9621 |
| 204 | w | 1·555$_5$ | 316 | vw | 0·9404 |
| 300 | m | 1·487 | 405 | wm | 0·9384 |
| 213 | w | 1·457 | 324 | m | 0·9256 |
| 205 | wm | 1·370$_5$ | 218 | ms | 0·9127 |
| 214 | w | 1·331$_5$ | | | |
| 220 | wm | 1·287$_5$ | s = strong; ms = moderately strong; |
| 116 | ms | 1·2618 | m = moderate; wm = weak moderate; |
| 304 } 311 } | wm | 1·2267 1·2247 | w = weak; vw = very weak; vvw = just visible. |
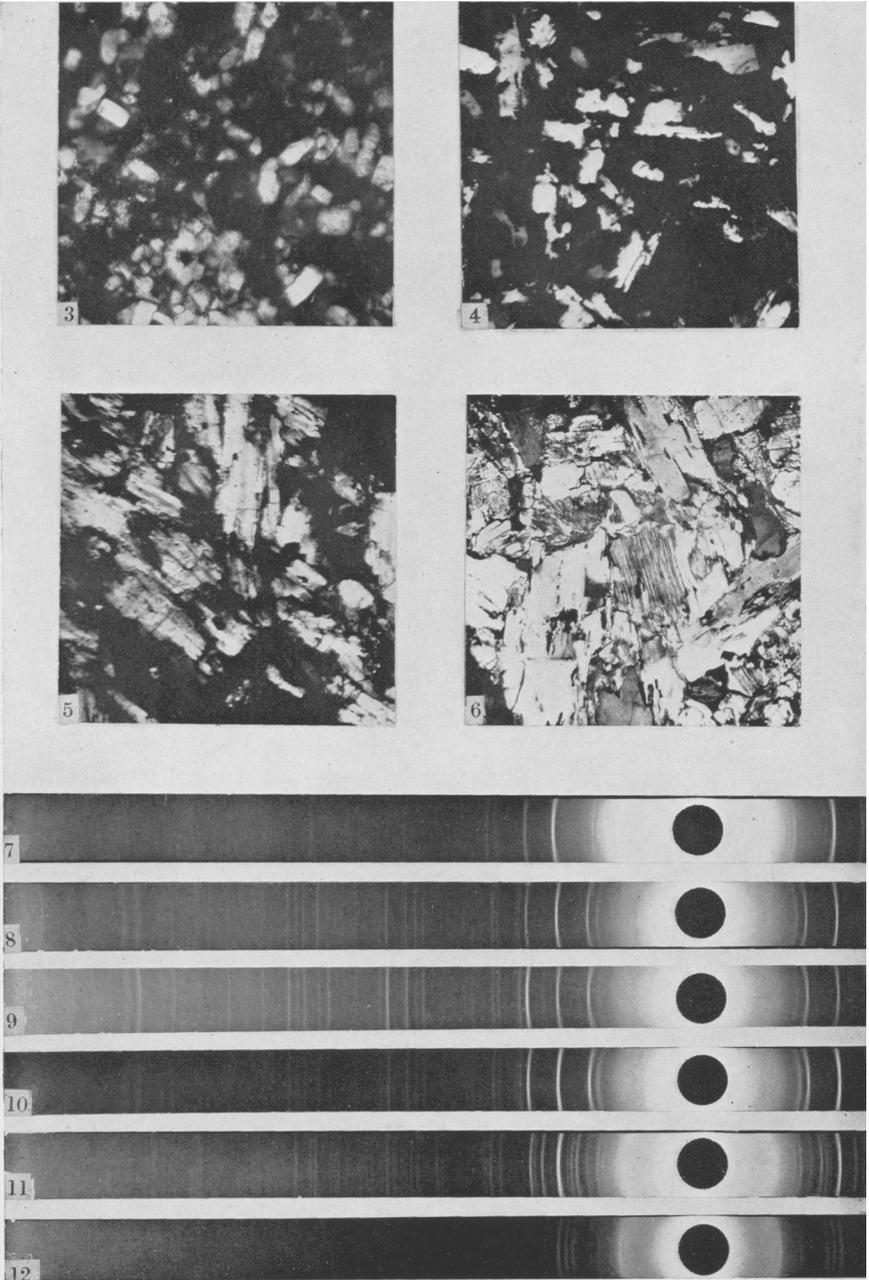
G. R. Rigby and H. M. Richardson: Artificial Kalsilite, &c.