

179. *A New Calcium Silicophosphate.*

By GUNTER NAGELSCHMIDT.

IN the course of a mineralogical investigation of a typical series of modern basic slags which had been tested as phosphatic fertilisers in field and pot culture experiments (Crowther, *J. Roy. Agric. Soc.*, 1934, **95**, 1), a new material was found as a major constituent of some open-hearth slags with citric acid solubilities between 40 and 80%. Although at least 80% of the material in commercially ground basic slags is guaranteed to pass through the British Standard Test Sieve, mesh number 100, a few individual particles may be as large as 0.5 mm. in diameter and a small fraction is below the range of microscopic visibility. Most of the grains are heterogeneous; they contain inclusions, different materials are intergrown, and it is therefore very difficult to isolate the pure components, although these can often be recognised and identified by microscopical and microchemical methods. In the present work it was possible to isolate the new compound in three stages.

(1) A suitable grain size group of about 0.2—0.02 mm. diameter was separated by sieving and sedimentation in water saturated with calcium carbonate. (2) A magnetic separation was carried out by using Hallimond's separator (*Min. Mag.*, 1930, **22**, 377),* a non-magnetic fraction being obtained in which all the grains were more or less free from dark inclusions. (3) A gravity separation was effected by repeated centrifuging with methylene iodide-benzene mixtures. The new compound was found to have $d^{20^\circ} 3.035 \pm 0.005$.

Optical Properties.—The material is colourless, and biaxial positive. The angle of the optical axes is very small. The largest and the smallest refractive indices observed with sodium light are $n_\gamma 1.661$ and $n_\alpha 1.652 \pm 0.002$. The grains frequently have two opposite parallel edges with straight extinction along these edges. No other crystallographic boundaries occur, and the crystal symmetry is unknown, but cannot be higher than orthorhombic.

Chemical Composition.—From 25 g. of slag the above method of separation afforded a 0.5 g. fraction which seemed to be sufficiently pure for chemical analysis, although it still contained a small percentage of foreign materials. Analyses made on 127 and 234 mg. gave the results shown

* The author is indebted to Prof. P. G. H. Boswell for permitting him to use this apparatus at the School of Mines of the Imperial College of Science and Technology.

in Table I, (i) and (ii) respectively, which give $\text{CaO} : \text{P}_2\text{O}_5 : \text{SiO}_2 = \text{approx. } 7 : 1 : 2$. If a recalculation is made on this basis it appears that the analysed material contained 92% of this compound, contaminated with tricalcium silicate and some spinelloid material. In view of this contamination and the fact that the analyses account only for 97% of the material, the formula of the new compound cannot be established with certainty, but $7\text{CaO}, \text{P}_2\text{O}_5, 2\text{SiO}_2$ seems the most probable.

Körber and Trömel (*Arch. Eisenhüttenw.*, 1933, 7, 7), investigating the ternary system $\text{CaO}-\text{P}_2\text{O}_5-\text{SiO}_2$, found two ternary compounds. The first had the composition $5\text{CaO}, \text{SiO}_2, \text{P}_2\text{O}_5$ and was identical with silicocarnotite, which has long been known as the main constituent of basic Bessemer slags. To the second compound they ascribed the composition $9\text{CaO}, \text{P}_2\text{O}_5, 3\text{SiO}_2$, but later (Trömel, private communication), $8\text{CaO}, \text{P}_2\text{O}_5, 2.5\text{SiO}_2$ was found to agree better with the data. It is not yet known, however, how far this second compound is able to form mixed crystals with the other components of the ternary system, and further synthetic work will be needed to elucidate this point. Both ternary compounds had citric acid solubilities above 95%.

The author is much indebted to Dr. Trömel for supplying him with a sample of his second ternary compound, which proved to have very similar optical properties to those described for the material $7\text{CaO}, \text{P}_2\text{O}_5, 2\text{SiO}_2$ isolated as detailed above. X-Ray powder diagrams* of the two materials proved to be identical, both in the position and in the intensities of the lines. The data are in Table II, together with comparable data for silicocarnotite, which gave a different pattern. This proves that the new compound is not a mixed crystal of silicocarnotite and dicalcium silicate. In view of the low crystal symmetry, the complex chemical composition, and the absence of suitably formed single crystals, no attempt was made to determine the crystal structure of the new material from the X-ray data.

TABLE I.
Chemical analysis of new compound.

	(i).	(ii).	Calc. for $7\text{CaO}, 2\text{SiO}_2, \text{P}_2\text{O}_5$.
CaO, %	58.3	58.4	60.0
P_2O_5 , %	19.9	20.0	21.6
SiO_2 , %	17.9	17.7	18.4
$\text{Fe}_2\text{O}_3 + \text{Al}_2\text{O}_3$, %	—	0.4	—
MgO, %	—	0.6	—
Total, %	96.1	97.1	100.0

TABLE II.
Powder diagrams of silicocarnotite (I), the new compound (II), and Trömel's synthetic material (III), taken with copper K- α radiation; interplanar spacings (d) and intensities (I) are recorded.

No.	(I).		(II).		(III).	
	d .	I .	d .	I .	d .	I .
1	4.58	w.	3.93	w.	3.93	w.
2	3.96	m.	3.51	w.	3.52	w.
3	3.60	v.w.	2.85	s.	2.86	s.
4	3.33	m.	2.70	s.	2.70	s.
5	2.99	m.	2.33	v.w.	2.33	v.w.
6	2.83	v.s.	2.22	v.w.	2.24	v.w.
7	2.61	v.s.	1.960	s.	1.961	s.
8	2.29	m.	1.862	v.w.	1.862	w.
9	2.18	m.	1.761	m.	1.761	m.
10	2.03	w.	1.668	w.	1.666	w.
11	1.958	w.	1.591	w.	1.590	w.
12	1.880	s.	1.562	w.	1.562	w.
13	1.812	w.	1.485	m.	1.487	m.
14	1.750	m.	1.346	m.	1.347	m.
15	1.691	m.	1.260	v.w.	1.262	v.w.
16	1.644	v.w.	1.220	v.w.	1.219	v.w.
17	1.538	w.	1.185	v.w.	1.185	v.w.
18	1.510	w.				
19	1.241	w.				
20	1.159	w.				
21	1.136	w.				
22	1.046	v.w.				
23	1.030	v.w.				

v.s. = very strong, s. = strong, m. = medium, w. = weak, v.w. = very weak.

* The author's thanks are due to Sir William Bragg and the Managers of the Royal Institution for facilities of the Davy Faraday Research Laboratory.

SUMMARY.

A new compound has been isolated from certain medium-soluble open-hearth basic slags, with a chemical composition approximating to $7\text{CaO}, \text{P}_2\text{O}_5, 2\text{SiO}_2$. It has d^{20} 3.035, n_γ 1.661, n_a 1.652 for sodium light, and is colourless and biaxial positive with a very small axial angle. X-Ray powder data are given. This material is almost identical with a synthetic calcium silicophosphate of approximate composition $8\text{CaO}, \text{P}_2\text{O}_5, 2.5\text{SiO}_2$ prepared by Trömel.

ROTHAMSTED EXPERIMENTAL STATION, HARPENDEN.

[Received, January 12th, 1937.]
