## XIII.—*Note on a Crystallized Slag isomorphous with Olivine.*

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Communicated by J. H. Collins.

THE crystals referred to were found in considerable quantity in the slags produced in Mr. Hollway's experiments on the reduction of metallic sulphides at Penistone, in July 1878.

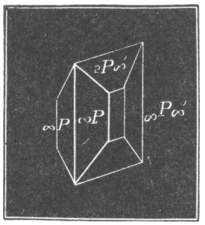
The experiments were carried out with ordinary Bessemer plant. Upon running the molten mass from the ladle into one of the ingot moulds the slag ran in a thick stream of perfect continuity, falling without noise a distance of some feet into the liquid portion below. The crystals occurred lining cavities in the partially cooled slag from which a portion of the molten material had been withdrawn.

Some of them were extremely well formed and they varied in size from about 1-100$^{th}$ to $\frac{1}{4}^{th}$ of an inch in length, and somewhat less in breadth and thickness.

After careful separation from contiguous substance the crystals were analysed in duplicate with the following results,—

| | I | II | Calculated on 13 FeO, FeS, 7 $SiO_2$ |
|---|---|---|---|
| $SiO_2$ | 28·99 | 29·06 | 29·08 |
| FeS | | 6·10 | 6·09 |
| FeO | | 61·34 | 64·82 |
| $Al_2O_3$ | | 60 | |
| Cu | | 14 | |
| MnO, ZnO | | 2·78 | |
| | | 100·02 | 99·99 |
| Sp. Gr | 4·19 | 4.22 | |

By adding together the basic oxygen and half the sulphur the sum is found to equal the oxygen of the $SiO_2$ showing that the presence of FeS cannot be accidental. If the analyses of slags I, II, III, V, of the July, 1878, Penistone experiments be similarly calculated into basic and acid oxygen, the fact is revealed that the sulphur takes part as a basic element in the constitution of the slag, so that we really have a silicate of a metallic sulphide.




Some of the crystals referred to have been examined by Dr. C. O. Trechmann, of Hartlepool, who states that they exhibit the forms shewn in the figure. He considers them to be artificial Fayalite, regarding the FeS present as a mere mechanical admixture, but its large quantity, and its proportion, *exactly* replacing one molecule of the ferrous oxide would seem to indicate that it is a true chemical compound. It differs from the mineral Helvin not only in crystallization but in having two atoms of metal to one of silica, whereas the latter contains seven of metal to three of silica.

I have tried the artificial formation of sulphosilicates, by passing $H_2S$ over metallic silicates. With 2 FeO $SiO_2$ I have not yet succeeded, the result I obtained being

$$2FeO\ SiO_2 + 2H_2S = 2\ FeS + 2H_2O + SiO_2$$

which is somewhat interesting.

The existence of sulphosilicates of iron was first suspected by Leplay, but he was unable to prove the hypothesis he enunciated. He observed that slags produced in the smelting of copper ores by the Swansea process invariably contained more sulphide of iron than could be accounted for by the presence of entangled regulus. The following examples may be cited to show how certain metallic sulphides may play the part of basic oxides in these artificial silicates. In the Penistone experiments crystalline homogeneous slags were produced of the orthosilicate type, which should contain therefore equal quantities of oxygen in acid and basic combination according to the formula $2M''O, SiO_2$. Now it appears from the analyses made by Mr. J. E. Stead and myself that there is a slight deficit in the amount of the basic oxygen which is almost exactly compensated for by adding to it half the percentage of sulphur (O = 16 replaced by S = 32) found to be present.

In the following analysis by Mr. J. E. Stead, it will be seen that the total oxygen found in the bases amounts to 14·382 per cent. In the operation in which this slag was produced the regulus obtained contained 15·8 per cent. of copper and 21·96 per cent. of sulphur. Casting out by means of these data the amount of sulphur present as regulus in the slag estimated on the 0·16 per cent. of copper present, we find we have to subtract 0.223 per cent. of sulphur from the sulphur found; 3·39 per cent − ·223 per cent. = 3·167 per cent. which represents the sulphur replacing oxygen in the sulphosilicate. The equivalent of this in oxygen is 1.583 per cent.

| | | | | |
|---|---|---|---|---|
| Iron Protoxide .. .. | 53·30% | Oxygen = | 11·844% | |
| ,, Peroxide .. .. | 3·00 | ,, = | 0·900 | |
| Iron comb. with Sulphur | 5·79 | | | |
| Copper ,, ,, ,, | 0·16 | | | |
| Lead .. .. .. .. | 0·12 | | | |
| Zinc Oxide .. .. .. | 1·15 | ,, = | 0·269 | 14·382% |
| Arsenic .. .. .. | trace | | | |
| Manganese Oxide .. | 0·32 | ,, = | 0·071 | |
| Alumina .. .. .. | 2·15 | ,, = | 1·000 | |
| Lime .. .. .. .. | 0·40 | ,, = | 0·114 | |
| Magnesia .. .. .. | 0·46 | ,, = | 0·184 | |
| Sulphur .. .. .. | 3·39 | | | |
| Silica .. .. .. .. | 29.90 | Oxygen = | 15·933% | |
| | 100.14 | | | |

| | |
|---|---|
| Basic oxygen present .. .. .. .. | 14·382% |
| Basic sulphur ,, Calculated into oxygen .. .. .. | 1.583 ,, |
| | 15·965% |

The oxygen calculated from 29·90% $SiO_2$=15·933%

Similarly in a second analysis by the same analyst analogous results are obtained on calculation.

| | | | | |
|---|---|---|---|---|
| Iron Protoxide .. .. | 54·62% | Oxygen = | 12·138% | |
| ,, Peroxide .. .. | 3·71 | ,, = | 1·113 | |
| Iron comb. with Sulphur | 4·27 | | | |
| Copper ,, ,, ,, | 0·22 | | | |
| Lead .. .. .. .. | 0·10 | | | |
| Zinc Oxide .. .. | 1·75 | ,, = | 0·348 | 14·927% |
| Arsenic .. .. .. | trace | | | |
| Manganese Oxide .. | 0·37 | ,, = | 0·082 | |
| Alumina .. .. .. | 0·06 | ,, = | 0·960 | |
| Lime .. .. .. | 0·37 | ,, = | 0·106 | |
| Magnesia .. .. .. | 0.45 | ,, = | 0·180 | |
| Sulphur .. .. .. | 2.55 | | | |
| Silica .. .. .. | 30·05 | Oxygen = | 16·027 | |
| | 100·52 | | | |

The regulus produced contained 16·6 per cent. of copper and 23·5 per cent. of sulphur: 0·22 per cent. of copper in slag corresponds to ·311 per cent. reguline sulphur.

| | |
|---|---|
| Total oxygen of Bases .. .. .. .. .. | 14·927% |
| Oxygen replaced by Sulphur = $\frac{2·55—·311}{2}$ | 1·119 |
| | 16·046% |
| Oxygen of Silica .. .. .. .. .. | 16·027% |

It is probable that sulphur exists in blast and puddling furnace slags in the form of sulphosilicate. It is well known that manganese exercises an affinity for sulphur in the presence of silicious fluxes, which calls to mind the fact that the only natural sulphosilicate known is that of manganese.