

ON THE DETERMINATION OF SILICA IN BLAST-FURNACE SLAG.

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THAT silica is not rendered completely insoluble by one evaporation to dryness with hydrochloric acid, has long been recognized. Several evaporations, even, may not dehydrate traces of silicic acid. Moreover, unless the temperature of drying be carefully regulated, some of the silica may recombine with the bases present and either form highly insoluble silicates, or else go into solution on subsequent treatment with hydrochloric acid. Boiling, concentrated sulphuric acid, on the other hand, is a very efficient agent for the dehydration of silicic acid, Drown's much-used method for silicon in pig iron making use of the fact.

It is the purpose of this article to show that the method of dehydration of silicic acid by sulphuric acid forms a most accurate method for the determination of silica in blast-furnace slags. This arises not only from the fact of the positive and quick production of insoluble silica; but, what is probably more important, from the very complete decomposition of certain constituents of many slags, and the production of a purer silica than can be otherwise obtained.

Those constituents of slags which have most contributed to inaccuracy in the determination of silica, are spinel (magnesium aluminate)¹ and certain complex titanium compounds. On examples of such slags, accurate determinations of silica could not be made either by direct solution in hydrochloric acid or by solution in hydrochloric acid after fusion with sodium carbonate; yet the silica was readily determined by application of the simple process described below.

Pure spinel is thoroughly decomposed by fusion, at a high temperature, with a large excess of sodium carbonate. But spinel, when associated with slag, is only decomposed thus with great difficulty.² A slag containing as much as five per cent. of spinel residue by ordinary methods, is nevertheless easily decomposed by boiling concentrated sulphuric acid. Considera-

¹ Shimer: This Journal, 16, 501.

² Frank Firmstone: Trans. A. I. M. E., 24, 498 et seq., 892 et seq. (The residues there obtained were separated after fusion with sodium carbonate.)

ble experience with a slag, prone to spinel formation, has never shown, even under most favorable conditions for spinel formation, more than this amount in the suddenly cooled slag.

When pure spinel is treated with boiling concentrated sulphuric acid, it "sets" to a hard mass; the surface of the mass being changed to sulphates of magnesium and aluminum, that, being insoluble in the concentrated acid, prevent further decomposition of the spinel. Upon treatment with water these sulphates dissolve. The operation being repeated, more spinel is decomposed; and so on until complete decomposition results.

When the spinel is associated with slag, however, it is decomposed by one treatment with sulphuric acid, probably because of each small particle of spinel in the finely ground slag being separated from the others. Thus, a very difficultly decomposable slag was found to contain about three and one-half per cent. of spinel; but upon determining silica by the method to be given, the silica was found to be almost pure, and the impurities contained no magnesia.

It might be thought that to treat the impure silica from such slags with hydrofluoric acid and weigh the residues would suffice to accurately estimate the silica. This would be the case were it not for the fact that these spinel residues usually contain other compounds. When these compounds contain, as they usually do, some bodies that are changed to new bodies by treatment with hydrofluoric and sulphuric acids, accurate results can only be obtained when the subsequent ignition causes a reversion to the former conditions.

Thus, suppose an impure silica obtained in the course of analysis and containing, among other impurities, an insoluble compound of titanium, aluminum, magnesium, iron, and potash or soda. This impure silica being treated with hydrofluoric and sulphuric acids, the silica would evaporate as silicon tetrafluoride and the bases change to sulphates. Upon igniting strongly, the aluminum, magnesium, and iron would again revert to the original conditions as oxides; but not so with the alkalis. They would either volatilize at a white heat or else remain and retain most of their sulphur trioxide. It is obvious that, under such circumstances, erroneous results for silica would necessarily occur. Below is given a case from actual experience.

Slag No. 1944 was found to give by ordinary methods of analysis, as follows :

	Per cent.
Silica and impurities	35.42
Impurities determined by treatment with hydrofluoric and sulphuric acids	5.88
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Silica	29.54

This slag was very exceptional, for although as much as one per cent. of the slag had often been found in the impure silica, never before so much as 5.88 per cent. For the present 29.54 per cent. was considered to be the true proportion of silica in the slag. But in some investigations on spinel, it was noticed that the spinel residues were notably soluble in hot concentrated sulphuric acid. Taking advantage of this fact, the silica was redetermined in this slag, using the new method, with the following result :

	Per cent.
Silica and impurities	31.20
Impurities determined by treatment with hydrofluoric and sulphuric acids	0.20
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Silica	31.00

In other words, the former result had been about one and one-half per cent. too low—a very large variation from the truth. A special investigation on this slag showed that after treatment with boiling hydrochloric and hydrofluoric acids there still remained a residue amounting to 3.81 per cent. of the slag. This residue was not entirely decomposed by sulphuric acid (owing probably to changes produced by igniting to burn off filters) ; but, as the above analysis shows, it was readily decomposed by sulphuric acid as it existed in the slag.

The method is as follows : One-half gram of finely ground slag is placed in a four-inch casserole. Cover with cold water (about three cc.) and stir to break up lumps. Then pour into the casserole ten cc. concentrated hydrochloric acid, stirring vigorously to prevent sticking to the bottom.

As soon as the slag seems dissolved as much as it will, and before it has set to a jelly, pour in forty cc. sulphuric acid (one volume concentrated acid to one volume water), stir well, wash off stirring rod, and then cover solution with a funnel.

The funnel should have fused edges and be of such size as to rest upon the sloping inside of the casserole and set down above to the solution.

Place the casserole on a wire gauze and boil rapidly until fumes of sulphur trioxide begin to come from under the edges of the funnel. Cool, dilute somewhat, and clean off the funnel. Add about ten cc. hydrochloric acid and dilute until the casserole is as full as it can be conveniently. Cover with watch-glass and boil gently one minute. Filter on pump. Wash five times with hot hydrochloric acid (sp. gr. 1.10) and five times with hot water. Burn and weigh. The silica is remarkably pure. On "chilled" slags the impurities are from 0.05 to 0.20 per cent.

This method has been carefully compared with a method consisting of two evaporations to dryness with hydrochloric acid, regulating the heat so as not to exceed 120° C., and finally purifying the silica with hydrofluoric acid. The results are generally quite close (the only exceptions being such cases as cited above, where only the sulphuric acid method could give accurate results), the sulphuric acid method giving results somewhat higher, due to the more complete dehydration of silicic acid.

In no case has there been found any evidence of calcium sulphate in the silica when the method is carried out as directed.

TABLE OF RESULTS.

Hydrochloric acid evaporation.	Sulphuric acid evaporation.
36.00	36.06
35.52	35.62
34.24	34.74
35.76	35.96

The time necessary is about one and one-half hours, and there is very little attention required. "Chilled" slag is best suited, but the method will be found successful on many slowly cooled slags that are very insoluble in hydrochloric acid. Unfortunately, the method is only useful for the determination of silica. Attempts to determine readily alumina and lime in the filtrate from the silica have all failed. Results are much too low.

It is worthy of note that the silica obtained is very dense and hard. This is an advantage, in that there is little danger of loss of the silica, due to its being thrown out of the crucible by the gases escaping while the filter is charring. With the silica

ordinarily obtained, this mechanical loss is very apt to occur. The silica obtained by this method is, however, more difficult to decompose by treatment with hydrofluoric acid. It is much less hygroscopic and weighings are thus more accurately made.

For as many slags as have been investigated there is claimed for the above method (1) greater accuracy due to more complete dehydration of silicic acid, and thorough decomposition of certain slag constituents, and (2) greater rapidity and ease of execution than for other methods of about equal accuracy.

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THE DETERMINATION OF LEAD IN LEAD ORES.¹

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IN the wet assay of lead ores, the general mode of procedure seems to be to precipitate the lead as a sulphate by dissolving the ore in a mixture of sulphuric and nitric acids and evaporating until the solution is free from the latter acid. The residue, consisting of the precipitated lead sulphate and gangue, is collected upon a filter paper and, after washing, is dissolved in either ammonium tartrate or acetate or in sodium thiosulphate; then precipitated as an oxalate or chromate and determined volumetrically, or precipitated as a sulphide and estimated gravimetrically. Another way is to ignite the residue of lead sulphate and gangue and weigh. Then treat with ammonium tartrate or acetate, and collecting whatever residue remains, ignite and weigh. The difference between these two weights is taken as lead sulphate.

Of these methods the first is rather inaccurate.² The third is rather slow, and both are inapplicable when calcium, barium, and strontium are present. The second is the most accurate of the three outlined above, but is also the slowest.

While recently working upon some specimens of galena, the writer thought of a simple method for determining the amount of lead in this mineral, and in lead ores in general. Like two of the above methods, it fails in accuracy when barium, strontium, and small amounts of calcium are present, since these

¹ Read at the meeting of the New York Section, March 5, 1897.

² See Sutton: "Systematic Handbook of Volumetric Analysis," Sec. 66, 1 and 2.