These were in general of the same shape as the etch figures and increased rapidly in size as the etching proceeded. A certain percentage of these crystals was stationary and occasionally a moving crystal was seen to stop suddenly, as though it had become attached to the glass surface. Both the floating and stationary crystals grew rapidly in size as the etching proceeded. When the plate was then cleaned, etch figures, of the size and shape of these stationary crystals, were observed in their places. From this it appears that the etch figure is produced by the protective action of crystals which are formed as the etching proceeds.

The composition of the deposited crystals was then investigated. From the fact that etch figures were formed on fused silica (Fig. 18), it was suspected that the crystals consisted of ammonium fluosilicate. Ammonium fluosilicate was therefore prepared by partially neutralizing fluosilicic acid with ammonium hydroxide. A finely crystalline precipitate was obtained, which, on examination under the microscope, appeared identical with the crystals formed during the etching process. These are illustrated in Fig. 19. Analysis showed them to be ammonium fluosilicate:

Calculated for $(\text{NH}_4)_2\text{SiF}_6$	FOUND
Per cent NH_3 19.09	18.76 and 19.04

This substance crystallizes in the regular system, and, in general, the individual crystals are cubes modified by octahedral and dodecahedral faces.

As has been pointed out, the etch figures result from two simultaneous actions: the solution of the glass, and the growth of the crystal which is in mechanical contact with the glass surface. The etch figures are therefore neither pseudomorphs nor casts; and, consequently, can not be expected to be exact duplicates of the crystals. They are essentially silhouettes of crystals which are constantly growing. The figures often show striations normal to the direction of growth of the crystal (Fig. 13), which suggests that possibly the crystal growth or perhaps the solvent action is subject to rhythmic disturbances.

It has been observed that the etch figures are commonly hexagonal in appearance and it might be expected that other shapes should predominate if they were the result of the protecting action of cubic crystals. It is evident that, if the octahedron were in contact with the glass surface, and if the cubical and dodecahedral faces were to develop simultaneously, a hexagonal figure should result. This is apparently what occurs in the majority of cases, and no explanation, except that of habit, can be offered to account for it. It is to be expected that etch figures of triangular, square and octagonal outline should also be formed, and these figures are nearly always observed in limited numbers (Figs. 12, 13, 14, 18 and 20).

If this theory is correct, it is to be expected that the presence of other metals which form insoluble fluosilicates, will produce characteristic etch figures in accordance with their crystalline habit. This is illustrated in the case of the potash-lead glass (Fig. 15); the etch figures are decidedly characteristic of potassium; and, so far as the writer has observed, *they are*

always produced by an etching solution which contains potassium, irrespective of the composition of the glass. The laboratory glasses (Figs. 16 and 17) also illustrate some characteristic figures. These glasses were free from potash, but contained considerable percentages of boric acid, alumina and zinc oxide, and are extremely resistant to the action of the etching solution. As will be seen from the photomicrographs, the habit of these figures is "tabular" with square and triangular forms predominating, but six- and eight-sided figures are not uncommon. This theory also indicates that, if the etching solution contains no substance which produces insoluble fluosilicates or fluorides, the glass should be dissolved evenly, as with hydrofluoric acid alone, and without characteristic etch figures. This was found to be the case when the solution consisted of the acid fluorides of sodium, lithium, aniline, pyridine, zinc and urea. It is therefore apparent that the glass, *per se*, is dissolved evenly and as a whole by the etching solution, *whatever the composition of the solution may be*; and that the matness and etch figures result from a secondary protective action of whatever insoluble materials are formed in contact with the glass surface. The character of the etch figures will be determined by the most insoluble substance deposited; and this perhaps explains the results obtained with acid ammonium fluoride and the potash glass, and also with the borosilicate laboratory glass.

SUMMARY

From the foregoing it is concluded that:

I—All glasses dissolve evenly in acid fluoride solutions.

II—Matt etches and etch figures are obtained only when insoluble substances are formed in contact with the glass surface, and when the solution of the glass in such local areas is thereby prevented.

III—When the etching solution is acid ammonium fluoride, crystals of ammonium fluosilicate form the protecting material.

IV—The etch figures result from a solution of the glass and the growth of crystals, deposited from the solution, in contact with the glass surface. Both reactions take place simultaneously.

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THE DETERMINATION OF IRON IN GLASS SAND

By JOHN B. FERGUSON

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One of the absolute essentials in the manufacture of optical glass is a supply of good glass sand, and one of the indispensable attributes of such a sand is a minimum iron content. In searching for such a sand one is compelled to rely on chemical analysis, and now that the problem of optical glass has become a question of national importance it is essential that no errors be made in the seemingly simple determination of the iron in a sand.

In the past, sand analyses generally have shown too low an iron content and since the Geophysical Laboratory has taken up the problem of optical glass, this has been the source of some rather vexatious

delays. In fact it has been necessary for us carefully to re-analyze practically all the sands under consideration, and it was while carrying out some of these analyses that the writer thought he had discovered the source of the trouble.

The usual method may be thus described: the sand sample of about 5 g. is digested with hydrofluoric and sulfuric acids repeatedly until all the silica disappears and no gritty particles remain. The heat is then increased until all the hydrofluoric acid is driven off and copious fumes of sulfuric anhydride arise. The vessel is cooled, its contents taken up with water and filtered. The iron is determined in the filtrate.

When a qualitative test¹ alone is desired, the sand is dissolved in hydrofluoric acid, and potassium ferrocyanide is added to the solution, a blue color indicating iron.

Both of these methods of attack assume that a sand is completely decomposed with hydrofluoric acid, and it is to this assumption that the writer wishes to draw attention. From a theoretical standpoint its validity is doubtful since a glass sand often contains such minerals as magnetite, ilmenite, tourmaline, staurolite, etc., minerals that do not break up readily under this treatment, and in practice the writer has found that in so-called good sands, sands in which the iron is practically all present in the heavy minerals, the greater part of the iron was lost under such treatment. Two cases may be cited as illustrations:

I—A sample of sand from Crystal City, Missouri, was analyzed in the usual manner and found to contain less than 0.01 per cent Fe_2O_3 , a result in agreement with the analyses of the sand usually reported. The microscopic examination, for which I am indebted to Dr. H. E. Merwin, of this laboratory, raised some doubt as to the correctness of previous results and another analysis was made: the residue left after filtration was fused with iron-free potassium pyrosulfate and the cake so obtained dissolved in dilute sulfuric acid and added to the original filtrate. This time the iron content was found to be approximately 0.03 per cent, and a third analysis confirmed this latter figure.

II—A sand from Altmont Springs, Florida, was given the same treatment as that given in Case I and then in addition boiled with 1 : 1 hydrochloric acid. The solution so obtained was found to contain practically no iron. Upon careful examination the presence of staurolite grains still undecomposed was discovered and when these were broken up by fusion with sodium carbonate for half an hour the iron content was found to be 0.021 per cent of the sand.

Further evidence on this point may be deduced from the analyses presented in a report on glass-making material by Ernest F. Burchard.² The American Window Glass Company and the Pittsburgh Plate Glass Company each submitted to him four sand analyses. The American Window Glass Company's analyses show for the Fe_2O_3 content—a trace, 0.006,

0.011 and 0.021 per cent, respectively, and of these sands they say: "No. 1 is suitable for the highest grades of glassware and flint glass. Nos. 2 and 3 are suitable for tableware, plate-glass, chimneys, prescription ware, etc., and No. 4 is used for window glass." The Pittsburgh Plate Glass Company's analyses indicate 0.003, 0.002, 0.0024, 0.0036 per cent, respectively, for the same sands and their comment is: "For sands with analyses comparable with the above, no decolorization is attempted in manufacturing plate glass. Sand containing more iron than is shown in the tables may be used in making green glass bottles and cheap glassware or with the addition of decolorizing agents in making window glass." Such comments and analyses do not agree. The coloring indicated by the comment corresponds to much more iron than is shown in any one of the eight analyses, and since the glass-makers watch their products with much more care than their raw materials the analyses must be at fault.

In this connection it is interesting to note that Henry B. Kummel and R. B. Gage,¹ upon removing the heavy minerals from some New Jersey sands, obtained analyses of the purified material comparable with those quoted above and their experience with these sands led them to the belief that most of the iron was present in such minerals: "The amount of iron and titanium found by analysis is readily explained by these minerals in the sands and one cannot question the conclusion that the iron content which is especially detrimental is due solely to these minerals, particularly ilmenite."

Before starting such an analysis it would be best for the analyst to obtain a microscopic examination of the sand and base his method of attack on this information. Failing this, the following procedure is recommended as one in which the analyst may have reasonable confidence.

PROCEDURE

Weigh out 5 g. of the sand in a large platinum crucible or small basin; moisten with 5 cc. 1 : 1 sulfuric acid and then add 40 cc. hydrofluoric acid. Evaporate until white fumes of sulfur trioxide begin to be given off; cool, and if upon examination silica can be seen, add more hydrofluoric acid and repeat the evaporation. Two such evaporations generally suffice, but if necessary a third should be made. The use of some form of radiator similar in principle to the well known survey radiator is recommended and may be easily improvised. After the final evaporation the temperature is increased until copious fumes of sulfur trioxide are given off and all the hydrofluoric acid removed. The crucible is cooled, its contents diluted with distilled water and filtered. The black residue remaining on the filter will consist principally of carbonaceous matter derived from the hydrofluoric acid which is usually kept in ceresin bottles, and this carbonaceous matter will prevent the analyst from ascertaining the completeness of the decomposition. The filter containing this residue, without washing,

¹ Geological Survey, *Bull.* 285 (1906), 454.

² "The Requirements of Sand and Limestone for Glass Making," Geological Survey, *Bull.* 285 (1906), 454.

¹ Report of the State Geologist, New Jersey, 1906.

is removed from the funnel, placed in a small platinum crucible, dried and ignited. The funnel is carefully rinsed with distilled water, the rinsings being allowed to run into the filtrate. After ignition the residue is fused with a little iron-free potassium pyrosulfate and the cake so obtained is dissolved in dilute sulfuric acid. If no residue is left the decomposition is complete and the two solutions may be combined, and the iron then determined in the resulting solution. If dark particles may still be seen, and this will be the case if staurolite is present, they are filtered off, ignited and fused with iron-free sodium carbonate in a platinum crucible. Upon treating this fusion with dilute sulfuric acid careful examination should show no black particles and after filtering to remove any insoluble sulfates the three filtrates are combined and the iron determined in this resulting solution.

The writer prefers to reduce the iron with stannous chloride and then to titrate with potassium bichromate, determining the end-point electrometrically as suggested by Joel H. Hildebrand,¹ and for this reason dissolves the fusions in 1:1 hydrochloric acid instead of sulfuric acid. The exact conditions required by this method have been studied by Hostetter and Roberts of this laboratory, and the writer wishes to thank them for the information and assistance they have given him.

Other well known methods would probably give equally good results.

In making analyses such as these the purity of one's platinum and reagents becomes a question of prime importance. While careful blank determinations will eliminate errors due to the latter they cannot be relied upon in the case of the former and no iron-bearing platinum may be used.

It cannot be too strongly emphasized that no "Analyzed Chemical" can be relied upon without test for work such as this.

CONCLUSIONS

Before the correct iron content of a sand can be determined the sand must be completely decomposed. Simple treatment with hydrofluoric acid and sulfuric acid is not sufficient. Fusion of the residue with potassium pyrosulfate must be resorted to and even subsequent fusion with sodium carbonate in rare cases.

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THE FORMATION OF TRI-CALCIC ALUMINATE

By EDWARD D. CAMPBELL

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As early as 1883 Le Chatelier came to the conclusion that the two essential constituents of Portland cement were tri-calcic silicate and tri-calcic aluminate. All efforts to produce a sound cement of the empirical formula

¹ *J. Am. Chem. Soc.*, **35** (1913), 871.

failed, free lime always being found in materials of this composition. Later, Newberry suggested that the essential constituents were tri-calcic silicate and di-calcic aluminate and proposed the formula

Even this latter formula gives a mixture almost always containing some free lime, so that in practice it is customary to keep the lime ratio a little below that called for by the Newberry formula in order to produce a uniformly sound cement.

The existence of tri-calcic silicate as first suggested by Le Chatelier received a strong confirmation from the work of A. H. White,¹ and in 1915 essentially pure crystals 0.03 mm. in diameter were described by Shepherd, Rankin and Wright.² Later, by very slowly cooling a solution of di-calcic silicate and calcium oxide in $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$ as solvent, the author³ obtained crystals of essentially pure tri-calcic silicate 7 mm. in length.

Two facts in connection with tri-calcic silicate should be noted: (1) large crystals of tri-calcic silicate can be best obtained by slowly cooling a solution of di-calcic silicate and calcium oxide in $5\text{CaO} \cdot 3\text{Al}_2\text{O}_3$; (2) as pointed out by Le Chatelier, when tri-calcic silicate is treated with water, one molecule of calcium oxide readily forms calcic hydroxide, leaving a hydrated di-calcic silicate which gradually undergoes further hydrolysis. These two facts relative to the formation and behavior of tri-calcic silicate would suggest the idea that calcium oxide may, under suitable conditions, unite with di-calcic silicate to form crystals in which the calcium oxide would bear a relation to the di-calcic silicate exactly analogous to that borne by the water of crystallization to the hydrated salt with which it is united.

Essentially pure tri-calcic aluminate was prepared and its properties described in 1909 by Shepherd, Rankin and Wright.⁴ Some of the properties of tri-calcic aluminate were described in 1915 by Rankin and Wright⁵ as follows:

"This compound occurs in equant colorless grains 0.1 mm. and less in diameter, often hexagonal or rectangular in outline, with indications of imperfect cleavage after the octahedron or rhombicdodecahedron, crystal system, isometric; refractive index, $N_{na} = 1.71 \pm 0.001$; hardness, 6; fracture, conchoidal; luster, vitreous. Occasionally faint gray interference colors were observed and were evidently due to strain."

The experimental data from which Shepherd, Rankin and Wright drew their conclusions are shown in the accompanying diagram taken from the two publications mentioned. This diagram assumes that tri-calcic aluminate, composed of 37.78 per cent Al_2O_3 and 62.22 per cent CaO , is a stable phase in all mixtures containing less than 52.2 per cent Al_2O_3 and at all temperatures up to its melting point, $1535^\circ \pm 5^\circ$, at which point it "dissociates into CaO and liquid." It is stated that because of the dissociation at the melting point into CaO and liquid, pure tri-calcic aluminate is

¹ *THIS JOURNAL*, **1** (1909), 5.

² *Am. J. Sci.*, **39** (1915), 1; **29** (1909), 293.

³ *THIS JOURNAL*, **6** (1914), 706.

⁴ *Am. J. Sci.*, **28** (1909), 293.

⁵ *Ibid.*, **39** (1915), 1.