ON A MODIFIED METHOD FOR DECOMPOSING ALUMINOUS SILICATES FOR CHEMICAL ANALYSIS

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ABSTRACT

Evidence has been obtained that certain silicates of alumina and allied compounds, especially ceramic materials, can be decomposed for chemical analysis with relatively small amounts of Na₂CO₃. Satisfactory decomposition has been obtained by heating a 0.5 g sample with 0.6 g of Na₂CO₃ at 875°C for two hours.

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I. INTRODUCTION

The decomposition of aluminous silicates for chemical analysis is usually effected by fusing 1 part of the powdered sample with from 4 to 18 parts of Na₂CO₃. W. F. Hillebrand ¹ points out that "the larger amounts (of flux) introduce more impurity than the smaller and necessitate longer washing of precipitates," and that one of the disadvantages in the use of alkali carbonates is "the annoying interference of several grams of foreign fixed salts, which are most troublesome in that part of the analysis devoted to the separation of silica, alumina, iron, lime, and magnesia." In preparing certain silicates of a high alumina content for analysis, Lundell and Hoffman ² found it necessary to use approximately 18 parts of flux to 1 of sample, and they discuss at length the errors introduced by incomplete decomposition and the subsequent incomplete removal of fixed salts.

In addition to other recognized but infrequently used methods for decomposing silicates for analysis, the literature, especially that referring to patents, contains many suggestions for breaking up silicates to obtain, commercially, one or more of their individual constituents. Many of the suggested methods can not be used for analytical purposes because they involve the use of undesirable fluxes, or do not produce complete decomposition. However, some patents are based on decomposition effected by sintering siliceous materials with small amounts of Na₂CO₃. Furthermore, the decomposition of argillaceous limestones by heating them with small amounts of Na₂CO₃ is recommended by several authors.³ Hitherto, the use of relatively small amounts of flux has had but limited application in

³ Among these are P. W. Shimer, R. K. Meade, and W. F. Hillebrand.
analytical chemistry except in the cement industry, and P. H. Bates, of this bureau, suggested the possibility of extending this method to the analysis of ceramic materials. Since the literature does not contain, as far as the authors of this paper have been able to learn, specific references to the use of what might be called a “sintering method” for decomposing silicates for analysis (except, of course, the time-honored J. Lawrence Smith method for determining alkalies), a series of tests were made to determine the feasibility of using very small amounts of Na$_2$CO$_3$ for decomposing ceramic silicates.

II. EXPERIMENTAL PART

Initially, several attempts were made to decompose silicates for chemical analysis by heating 0.5 g samples with equal amounts of Na$_2$CO$_3$ in platinum crucibles over gas flames. Promising results were obtained, but it soon became apparent that heating at definite temperatures would probably give better results. Consequently, an electric muffle furnace was used, and temperatures were determined with a thermocouple connected to a portable potentiometer. Conditions were then modified by varying the amount of Na$_2$CO$_3$ used, the time of heating, and the temperature. It then became evident that the majority of samples tested decomposed readily after heating with Na$_2$CO$_3$ at about 875° C. for two hours.

The results obtained under several conditions and the silica and alumina content of the materials used are given in Table 1. For comparison, the table also contains the weights of the nonvolatile residues obtained after the samples had been decomposed by fusion, with the larger amounts of Na$_2$CO$_3$ ordinarily used. The materials referred to by numbers may be described as follows: Nos. 69, 70, 76, 77, and 78 represent standard samples prepared especially for the ceramic industry by the Bureau of Standards; of these No. 69 is bauxite, No. 70 is feldspar, Nos. 76, 77, and 78 are burnt refractories; No. 3 is a “flint clay”; No. 5 is a “bond clay”; No. 12 is a “crushed quartz”; No. 17 is a “siliceous brick”; M-1, M-2, and M-3 indicate routine samples which were analyzed after sintering, and their compositions and treatments are included in the footnotes to the table.

The sample and Na$_2$CO$_3$ were placed in a platinum crucible and thoroughly mixed by stirring with a glass rod. Intimate grinding in a mortar did not affect the final result materially, so in most of the work the simpler method of mixing was used. The addition of a few drops of alcohol and 1 or 2 ml of water to the two unmixed materials should be beneficial by bringing about more intimate contact between the clay and Na$_2$CO$_3$, but, on drying, segregation often occurs and produces undesirable results. However, a few good sinters were obtained after such a treatment.

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4 Attention is directed to the fact that temperatures in all parts of the muffle may not be the same as that indicated by a thermocouple placed in any one position.

5 Although the data contained in Table 1 are based on 2-hour treatments, some evidence was obtained that certain silicates can be decomposed in much less time.
<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Partial composition</th>
<th>Temperature and amount of Na₂CO₃ used</th>
<th>Nonvolatile residue after ordinary fusion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>SiO₂</td>
<td>Al₂O₃</td>
<td>825° C, 0.5 g Na₂CO₃</td>
</tr>
<tr>
<td>76</td>
<td></td>
<td></td>
<td>0.0139</td>
</tr>
<tr>
<td>77</td>
<td></td>
<td></td>
<td>0.0011</td>
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<tr>
<td>74</td>
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</tr>
<tr>
<td>75</td>
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</tr>
<tr>
<td>79</td>
<td></td>
<td></td>
<td>0.0020</td>
</tr>
<tr>
<td>80</td>
<td></td>
<td></td>
<td>0.0020</td>
</tr>
</tbody>
</table>

1 The figures in this column represent the average nonvolatile residues obtained from silica after the samples had been fused with Na₂CO₃ in the ordinary or generally recognized method. The figure in parentheses is the number of determinations on which the average is based.

2 Partially vitrified.

3 Temperature too low due to position of sample in muffle. (See footnote 4.)

4 0.3 g Na₂CO₃ used.

5 Fused.

6 Feldspar No. 70.

7 Glacial clay (66 per cent SiO₂, 14 per cent Al₂O₃, 55 per cent Fe₂O₃).

8 Kaolin (66 per cent SiO₂, 37 per cent Al₂O₃).

9 0.2 g Na₂CO₃ used.

10 0.5 g Na₂CO₃ used.

11 Shale (57 per cent SiO₂, 19 per cent Al₂O₃, 8 per cent Fe₂O₃).

12 1.0 g Na₂CO₃ used.

x Sinter unsatisfactory; discarded.
III. NATURE OF THE SINTER AND ITS SUBSEQUENT DECOMPOSITION

The word "sinter," as used in this report, refers to the product obtained after heating a mixture of the siliceous material with a small amount of Na₂CO₃. If the sample has been properly decomposed by the sintering treatment, the most desirable condition of the sintered material is that it be very friable or easily and completely broken up by very slight pressure with the flat end of a glass rod. Sinters have been obtained which after only very limited stirring were almost as finely divided as the original material. Less friable sinters are frequently obtained and they may also be quite vitreous or even distinctly glassy. If the sinter is very friable (as in the case of Nos. 69 and 78), no difficulty is encountered in decomposing it with water and HCl; if it is vitreous (Nos. 17 and 76), careful grinding with a glass rod before and during acid treatment is necessary; and if it is glassy (No. 70), digestion with water and HCl with frequent grinding readily effects decomposition. The addition of 1 or 2 ml of water to the sinters, previous to the addition of acid, promotes disintegration; this can be further facilitated by mild grinding with a blunt glass rod to break up the larger particles.

There are, of course, exceptions to the above conditions because at times vitrified or glassy masses are obtained which are so resistant to mechanical and acid treatment that they can not be satisfactorily handled. When these conditions are encountered, a change in either or both the amount of flux and temperature of sintering may yield a workable sinter, but a change in sintering conditions does not always appreciably affect the degree of decomposition. This may be seen in the data of Table 1, which indicate that the decomposition of sample No. 69 (bauxite) was quite satisfactory under a wide range of conditions. In this connection it should be stated that satisfactory results were obtained when bauxite was mixed with 0.5 g Na₂CO₃ and heated directly over the full flame of a Fisher burner. Furthermore, the sample of "kaolin" (footnotes 8, 9, and 8, in line M-1 of table) reacted well at 875° C. with 0.2 and 0.6 g Na₂CO₃.

The amount of insoluble residue, aside from the separated silica, remaining after the HCl treatment indicates qualitatively the degree of decomposition.⁶ The "degree of decomposition" (sometimes contracted to "decomposition") is measured by the amount of nonvolatile material remaining in the crucible after the dehydrated SiO₂ has been volatilized with HF in the presence of H₂SO₄. It was felt that this criterion could be used safely because in the ordinary analysis of silicates a few milligrams of residue are almost invariably found after volatilizing the dehydrated SiO₂. If, therefore, the residue after sintering was not excessive, decomposition was regarded as satisfactory. Hence, since the procedure following the weighing of the nonvolatile matter was not a part of this investigation, analysis was, in general, discontinued at this point.

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⁶ Bauxite and refractories of a high alumina content give a sludge on the addition of a little acid, which might be interpreted as very incomplete decomposition, but this sludge readily dissolves in excess acid.

⁷ G. E. F. Lundell suggests that a slight residue may be caused by a recombination of some of the constituents.
IV. RECOMMENDED PROCEDURE

In view of the foregoing statements, the following procedure is recommended for applying the sintering method to the decomposition of certain silicates for chemical analysis. Only the essential details of the sintering method will be given, and for other details the reader should consult the paper on the Analysis of Bauxite and of Refractories of High Alumina Content, by Lundell and Hoffman.  

Thoroughly mix 0.5 g of the powdered material and 0.6 g of powdered anhydrous Na₂CO₃ in a platinum crucible by stirring them with a glass rod for at least five minutes. Heat the covered crucible and its contents at 875° C. for two hours. Cool, add 1 or 2 ml of water, digest for about 10 minutes, and then stir, or grind if necessary, to break up all particles as completely as possible. Wash the contents of the crucible into a beaker or casserole, using not more than 50 ml of water. Heat to boiling, and with constant stirring, rapidly add about 20 ml of concentrated HCl (specific gravity 1.19). Crush any gritty particles that remain as much as possible with a glass rod and evaporate the solution to dryness. Finally heat at 105° to 110° C. for one hour to complete the dehydration of the SiO₂. Cool, add 20 ml of HCl (specific gravity 1.19), digest until effervescence of HCl ceases, add 100 ml of water, boil or digest with occasional stirring until all the aluminum compounds are in solution, filter through a 7 cm No. 40 Whatman or similar paper, and wash the precipitated SiO₂ first with hot dilute HCl (5 parts of concentrated HCl and 95 parts of water) and finally with hot water. Ignite the SiO₂ to constant weight and treat it with HF and H₂SO₄ in the usual way. Heat the residue and correct the initial weight of the SiO₂ accordingly. For more precise work, a second evaporation for residual SiO₂ should be made.

V. CONCLUSION

Although the work described in this paper is based on tests of a relatively few kinds of aluminous silicates it is thought that the method can be applied to other silicates by proper adjustments of the relative amounts of sample and Na₂CO₃ used, and the time and temperature of sintering. It should be especially useful to chemists who frequently analyze materials of the same general nature, because after having determined the particular conditions best suited to sintering their samples, the time required for thoroughly decomposing the sample will be shortened with no sacrifice of accuracy. In fact, the accuracy may be increased because the solvent action of excessive amounts of NaCl on silicic acid in HCl solution is largely eliminated, and the amount of foreign salts to be washed out of precipitates is greatly reduced.

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