Heats of Solution of Solid Solutions of Hexacalcium Dialumino Ferrite and Dicalcium Ferrite

By Edwin S. Newman

The heats of solution of members of the series of solid solutions between 6CaO.2Al2O3·Fe2O3 and 2CaO·Fe2O3 have been determined. Members of this solid-solution series are formed in cement clinker instead of the single compound 4CaO·Fe2O3·Al2O3, as formerly assumed. It has been shown that this assumption causes a negligible error in the latent heats at present used in estimating the glass content of portland cement clinker. It is pointed out, however, that the compositions and heats of solution of the glasses actually formed in portland cement clinker are still unknown. These quantities must be determined before the accurate estimation of the phase composition and glass content of commercial portland cement clinker is possible.

I. Introduction

For many years an objective of research on portland cement has been the correlation of the properties of the cements with their chemical constitution. This correlation requires the determination of the compositions of the mineral compounds in portland cement and the development of methods of calculating the relative amounts of each of these from the results of chemical analyses. Although notable progress has been made, errors in the estimates of the relative amounts of the minerals sometimes are large. These errors are partly due to inaccuracies in the estimate of the amount of glass, some of which is always present in portland cement. The determination of the glass content is based, in part, on values of the heats of solution of the individual minerals. The estimated glass content, therefore, will be in error unless the true substances present are recognized.

Recently there was announced the discovery in the ternary system CaO-Al2O3-Fe2O3 of a compound [1] hexacalcium dialumino ferrite, 6CaO.2Al2O3·Fe2O3. There was also found a complete series of solid solutions having the general formula 6CaO·xAl2O3·yFe2O3, in which x varies from two to zero and y simultaneously varies from one to three, the sum of x and y being always three. The extent of solid solution and the existence of the compound were unknown when many investigations of the constitution of portland cement clinker were made. As a first step in the possible revision of the method for the estimation of the glass content of portland cement clinker [2], the heats of solution in acid of the members of the solid-solution series have been determined.

II. Materials, Procedure, and Apparatus

The raw materials used in this study were reagent-quality chemicals: low-alkali calcium carbonate, ferric oxide, and hydrated alumina. Two mixtures were prepared which would have, after ignition, the compositions 6CaO·2Al2O3·Fe2O3 and 2CaO·Fe2O3. These basic mixtures were analyzed and their compositions adjusted. Quantities of these two materials were combined to give samples of about 10 g each of six other members in the solid-solution series. The samples, including those of the basic mixtures, were heated at 1,300°
C and ground in an agate mortar. This treatment was repeated until formation of the compounds was judged complete when the samples were examined under the petrographic microscope. After the final heating, the unground samples were stored in screw-cap vials in a desiccator. Just prior to the determination of the heat of solution, each sample was ground in a power-driven mortar for periods of from ½ to 2 hours.

The heats of solution were determined in a mixture of nitric and hydrofluoric acids. Ten milliliters of 48 percent HF were used together with sufficient 2.500 N HNO₃ to make a total weight of 648.5 g. The heat-of-solution calorimeter used in this work has been described in detail elsewhere [3]. The methods of calculation of heats of solution were those used in precision calorimetry [4].

III. Results and Discussion

The heats of solution and the compositions of the samples are given in table 1. The compositions are given in weight percentages of 6CaO·2Al₂O₃.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Compound formula</th>
<th>Heat of solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>6CaO·2Al₂O₃·Fe₂O₃</td>
<td>2CaO·Fe₂O₃</td>
<td>cal/g</td>
</tr>
<tr>
<td>wt percent</td>
<td>wt percent</td>
<td>647.2</td>
</tr>
<tr>
<td>100</td>
<td>0</td>
<td>646.2</td>
</tr>
<tr>
<td>85</td>
<td>15</td>
<td>646.4</td>
</tr>
<tr>
<td>72.0</td>
<td>28.0</td>
<td>646.6</td>
</tr>
<tr>
<td>60</td>
<td>40</td>
<td>avg...645.8</td>
</tr>
<tr>
<td>46.2</td>
<td>53.8</td>
<td>avg...646.0</td>
</tr>
<tr>
<td>30</td>
<td>70</td>
<td>avg...645.2</td>
</tr>
<tr>
<td>15</td>
<td>85</td>
<td>avg...644.9</td>
</tr>
<tr>
<td>0</td>
<td>100</td>
<td>avg...644.0</td>
</tr>
</tbody>
</table>

It was found that when plotted as a function of composition, the values of the heats of solution lay along a straight line (fig. 1). Average values only are shown in figure 1, as many of the determinations gave heats of solution too close together to plot individually.

![Figure 1](image-url)

**Figure 1.**—Heats of solution of the solid-solution series 6CaO·2Al₂O₃·Fe₂O₃—2CaO·Fe₂O₃ versus the composition expressed as weight percentage 2CaO·Fe₂O₃.

The closed circle is the value for 4CaO·Al₂O₃·Fe₂O₃ determined by Swenson, Herbert Inley, Einar P. Flint, Edwin S. Newman, and J. Arthur Swenson, Relation of compositions and heats of solution of portland cement clinker, J. Research NBS 21, 358 (1938) RP1135.
The equation \( H = 6.46C_aA_2F + 4.49C_2F \) represents the straight line chosen to portray the weighted data. In this equation, \( H \) is the heat of solution in calories per gram of any member of the solid-solution series and \( C_aA_2F \) and \( C_2F \) represent the composition of this member in percentages of \( 6CaO.2Al_2O_3.Fe_2O_3 \) and \( 2CaO.Fe_2O_3 \), respectively. This equation represents a line nearly parallel to the line of least squares and is drawn through the heats of solution of \( 6CaO.2Al_2O_3.Fe_2O_3 \) and \( 2CaO.Fe_2O_3 \). This line approaches Swenson’s value [5] for \( 4CaO.Al_2O_3.Fe_2O_3 \), determined with this calorimeter, somewhat more closely than does the least-squares line of the present data.

Many calculations have been made of the constitution and the heats of solution of cement clinkers [5], assuming complete crystallization into the compounds \( 3CaO.SiO_2 \), \( 2CaO.SiO_2 \), \( 4CaO-Al_2O_3.Fe_2O_3 \), and \( 3CaO.Al_2O_3 \). Frequently the calculations were made after correcting the CaO for uncombined lime [6]. The heats of solution thus calculated often agreed with the experimentally determined heats of solution of the incompletely crystallized clinker. Consequently, the calculated compound composition was sometimes incorrectly taken to represent the actual constitution of the clinker. The heats of solution of several of the compounds are relatively close. Incorrect assumptions as to the crystalline substances present in the clinker, therefore, can often appear to be verified by agreement between the observed and calculated heats of solution.

For example, clinker 25F in table 4 of the paper by Lerch and Brownmiller on the estimation of glass [2] had an oxide composition of 63.3 percent of \( CaO \), 5.0 percent of \( MgO \), 5.9 percent of \( Al_2O_3 \), 32 percent of \( Fe_2O_3 \), and 22.2 percent of \( SiO_2 \). The heat of solution of an “annealed,” i.e., completely crystallized, sample was 631.9 cal/g, determined experimentally. The calculated value, based on the incorrect assumption that the four compounds named in the preceding paragraph, together with \( MgO \), were the constituents, was 632.9 cal/g. If these values were the results of actual duplicate determinations of the heat of solution with the vacuum-flask calorimeter [7], they would be considered in excellent agreement [8]. However, if the heat of solution is calculated on the basis that \( 6CaO.2Al_2O_3.Fe_2O_3 \) is formed, as demonstrated by Swayze [1], instead of \( 4CaO-Al_2O_3.Fe_2O_3 \), the value 630.4 cal/g is obtained. This value is also in excellent agreement with the experimentally determined value, although the calculated amounts of \( 3CaO.Al_2O_3 \) and \( 2CaO.SiO_2 \) have been decreased by 5.5 and 3.5 percent, respectively. Furthermore, the amount of \( 3CaO-Al_2O_3.Fe_2O_3 \) has been increased by 4.3 percent, and 14.0 percent of \( 6CaO.2Al_2O_3.Fe_2O_3 \) having a heat of solution of 642 cal/g has been substituted for 9.7 percent of \( 4CaO.Al_2O_3.Fe_2O_3 \) having a heat of solution of 587 cal/g.

Because of the formation of \( 6CaO.2Al_2O_3.Fe_2O_3 \) instead of \( 4CaO.Al_2O_3.Fe_2O_3 \), the latent heats of crystallization of the liquids studied by Lerch and Brownmiller [2] are slightly in error. This difference is caused by the formation at crystalline equilibrium of different amounts of \( 2CaO.SiO_2 \) than assumed in their work. The observed differences between the heats of solution of the glasses and of the same material at crystalline equilibrium are the sums of the latent heats of the glasses plus the heat effects of the beta-to-gamma inversion of dicalcium silicate. The corrections to the observed differences in heats of solution to give the latent heats are therefore somewhat different than calculated by Lerch and Brownmiller [2].

The potential compound compositions at crystalline equilibrium and the heats of solution were recalculated for the nine liquid compositions given in reference [2]. The recalculated heats of solution agreed as well with the observed heats of solution as did those calculated on the former basis, the root-mean-square deviation being 1.7 cal/g compared with 2.1 cal/g. The differences in the calculated amounts of \( 2CaO.SiO_2 \) caused small differences in the latent heats of the glasses, amounting in the largest case to about 1.5 percent. Errors introduced from this cause into the estimation of the glass content of portland cement clinkers are insignificant compared with the normal errors of such calorimetry and with the errors introduced by the present lack of knowledge of the true composition of these glasses.

At present, the composition relations between the solid solutions of \( 6CaO.2Al_2O_3.Fe_2O_3 \) and the liquids in equilibrium with them are not known. It is therefore not possible to

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1 The heat of solution of \( 4CaO.Al_2O_3.Fe_2O_3 \) in the calorimeter used in the present work was 591 cal/g, differing from the value given in reference [2] by 4 cal/g. The value 666 cal/g for \( 6CaO.2Al_2O_3.Fe_2O_3 \) obtained in the present investigation was therefore reduced by 4 cal/g in recalculating the heats of solution.
estimate the compositions and quantities of the liquids formed at equilibrium in the system $2\text{CaO.SiO}_2 - 5\text{CaO.3Al}_2\text{O}_3 - 2\text{CaO.Fe}_2\text{O}_3 - \text{CaO} - \text{MgO}$. The heats of solution and latent heats of the glasses formed by cooling these liquids cannot be determined until their compositions are known. When this information is available, the phase composition and the glass content of commercial portland cement clinkers can be estimated more accurately than at present.

IV. Summary

The heats of solution of members of the series of solid solutions between $6\text{CaO.2Al}_2\text{O}_3.\text{Fe}_2\text{O}_3$ and $2\text{CaO.Fe}_2\text{O}_3$ have been determined. Members of this solid-solution series are formed in cement clinker instead of the single compound $4\text{CaO.} - \text{Fe}_2\text{O}_3.\text{Al}_2\text{O}_3$ as formerly assumed. It has been shown that this assumption causes a negligible error in the latent heats at present used in estimating the glass content of portland cement clinker. It is pointed out, however, that the compositions and heats of solution of the glasses actually formed in portland cement clinker are still unknown. These quantities must be determined before the accurate estimation of the phase composition and glass content of commercial portland cement clinker is possible.

The author is indebted to Mario Storlazzi and Leonard Bean for the chemical analyses and to L. A. Dahl for assistance in computation.

V. References

[1] Myron A. Swayze, A report on studies of:
   1. The ternary system $\text{CaO-C}_2\text{Al}_2\text{F}$.
   2. The quaternary system $\text{CaO-C}_2\text{Al}_2\text{F-C}_2\text{S}$.


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