CANADA

DEPARTMENT OF
ENERGY, MINES AND RESOURCES
MINES BRANCH
OTTAWA

UTILIZATION OF DIOPSIDE IN
THE MANUFACTURE OF GLASS

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JUNE 1974

Mines Branch Technical Bulletin TB 192

UTILIZATION OF DIOPSIDE IN THE MANUFACTURE OF GLASS

by

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SUMMARY

Due to the increasing cost and need for conservation of energy, diopside, $CaMg(SiO_3)_2$, was studied as a potential substitute for some of the materials used in the production of glass. The study was centered on the evaluation, from thermodynamic data, of the differences in heat capacity, heat of reaction and heat of mixing between diopside and stoichiometric quantities of $CaCO_3$, $MgCO_3$ and SiO_2. The results show that in the production of glass fiber 5.5 per cent of energy could be conserved by using diopside as a substitute material.

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Direction des mines

Bulletin technique TB 192

L'UTILISATION DE DIOPSIDE DANS LA
FABRICATION DE VERRE

par

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RÉSUMÉ

À cause du coût croissant et le besoin grandissant d'énergie, l'auteur a fait une étude sur le diopside $CaMg(SiO_3)_2$ comme produit potentiel de remplacement pour quelques matériaux utilisés dans la production du verre. Il a centré cette étude sur l'évaluation, des données thermodynamiques, des différences dans le pouvoir calorifique, la chaleur de réaction et la chaleur de mélange entre le diopside et les quantités stoechiométriques de $CaCO_3$, et SiO_2. Les résultats ont montré que dans la production de fibre de verre, 5.5 pourcent de l'énergie peut être conservé en utilisant le diopside comme produit de remplacement.

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INTRODUCTION

One of the major problems burdening the technology of glass is its low fuel efficiency. Past efforts to recover waste heat produced regenerative and recuperative furnaces. Even so, all glass-melting furnaces are relatively inefficient in their utilization of fuel. The recent increases in the cost of energy and the need for conservation of fuel have further emphasized the importance of thermal efficiency in the manufacture of glass.

While undoubtedly improvements can be made through increased use of insulation, more efficient regenerators, and better design and controls, savings in energy could also be realized by partial substitution of conventional raw materials with materials of different form. Most reactions in the formation of glass are either endothermic or exothermic. For instance, decomposition of $CaCO_3$ into CaO and CO_2 requires an appreciable quantity of heat. In contrast to this, less heat is needed if only CaO, rather than $CaCO_3$, is to be heated in a glass melt. This study therefore examined the possible thermal advantages which would result from the substitution in a glass batch of a naturally occurring mineral, diopside - $CaMg(SiO_3)_2$, for stoichiometric quantities of $CaCO_3$, $MgCO_3$ and SiO_2. A Canadian deposit of diopside with low iron and alumina content, such as may be found in the Grenville Series of the Precambrian formation, would be a suitable candidate.

DATA AND CALCULATIONS

The difference between the heat requirement of a conventional glass melt and one in which diopside replaces equivalent amounts of $CaCO_3$, $MgCO_3$ and SiO_2 can be established by summing the difference for individual components

and reactions. These are as follows:

(1) $\underline{CaCO_3}$

    (a) <u>Difference in heat requirement between $CaCO_3$ and CaO</u>
       <u>on heating from T_o to T</u>

Specific heats for $CaCO_3$ and CaO are given by Kelly[1]:

$$C_p(CaCO_3) = 19.68 + 11.89 \times 10^{-3}T - 3.076 \times 10^5 T^{-2} \text{ cal/mole } {}^oK \ldots (1)$$

$$C_p(CaO) \;\;\; = 10.00 + 4.84 \times 10^{-3}T - 1.080 \times 10^5 T^{-2} \text{ cal/mole } {}^oK \ldots (2)$$

$$\Delta C_p \;\;\;\;\;\; = 9.68 + 7.05 \times 10^{-3}T - 1.996 \times 10^5 T^{-2} \text{ cal/mole } {}^oK \ldots (3)$$

In general, the change of enthalpy at constant pressure is:

$$dH = C_p\,dt$$

Integrating

$$H = H_o + \int_{T_o}^{T} C_p\,dt \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (4)$$

Using the simplifying assumption that $H_o = 0$ and substituting

eq (3) in eq (4), one obtains:

$$H = 0 + \int_{T_o}^{T} (9.68 + 7.05 \times 10^{-3}T - 1.996 \times 10^5 T^{-2})dt$$

Integrating between T_o and T:

$$H = 9.68(T-T_o) + (1/2)\,7.05 \times 10^{-3}(T^2 - T_o^2) +$$

$$+ 1.996 \times 10^5 (1/T - 1/T_o) \ldots\ldots\ldots\ldots\ldots\ldots\ldots (5)$$

According to Perry[2], $CaCO_3$ decomposes at $1098\,{}^oK$. Substituting

the limits of integration, $T = 1098\,{}^oK$ and $T_o = 298\,{}^oK$ in eq (5),

one obtains

$$H = 11,193 \text{ cal/mole}$$

(b) Heat requirement for decomposition of $CaCO_3$

The heat of decomposition for the reaction $CaCO_3 \rightarrow CaO + CO_2$ can be obtained (for standard temperature, $298^\circ K$) from the difference of the heats of formation of products and reactants. For other temperatures, it can be calculated from the specific heats as follows:

$$C_p(CaCO_3) = 19.68 + 11.89 \times 10^{-3}T - 3.076 \times 10^5 T^{-2} \text{ cal/mole }^\circ K \dots (1)$$

$$C_p(CaO) = 10.00 + 4.84 \times 10^{-3}T - 1.080 \times 10^5 T^{-2} \text{ cal/mole }^\circ K \dots (2)$$

$$C_p(CO_2) = 10.34 + 2.74 \times 10^{-3}T - 1.955 \times 10^5 T^{-2} \text{ cal/mole }^\circ K \dots (6)$$

Subtracting (1) from the sum of (2) and (6), one obtains

$$\Delta C_p = 0.66 - 4.31 \times 10^{-3}T + 0.041 \times 10^5 T^{-2} \text{ cal/mole }^\circ K$$

By indefinite integration

$$\Delta H = \Delta H_o + \int \Delta C_p dT$$

$$= \Delta H_o + 0.66T - 2.155 \times 10^{-3}T^2 - 0.041 \times 10^5 T^{-1} \dots\dots\dots\dots (7)$$

The heat of reaction (ΔH) at $298^\circ K$ was measured by Roth and Chall[5] and found to be 42,470 cal/mole. Inserting this value in equation (7) at $T = 298^\circ K$, $\Delta H_o = 42,500$ cal/mole, the final equation is thus:

$$\Delta H = 42,500 + 0.66T - 2.155 \times 10^{-3}T^2 - 0.041 \times 10^5 T^{-1} \text{ cal/mole} \dots (8)$$

By substituting $T = 1098^\circ K$ in equation (8), the heat of reaction for the decomposition of $CaCO_3$ at $1098^\circ K$ is obtained:

$$\Delta H = 40,623 \text{ cal/mole}$$

The difference in the heat requirement between heating only CaO and that of heating and decomposing $CaCO_3$ is therefore:

$$11,193 + 40,623 = 51,816 \text{ cal/mole.}$$

(2) $MgCO_3$

According to Perry[3], the decomposition of $MgCO_3$ takes place at $650^\circ K$. As in the case of $CaCO_3$, one may calculate the difference in the heat requirement for heating only MgO and that for heating and decomposing $MgCO_3$ at $650^\circ K$. This difference, using the data by Kelly, amounts to 32,016 cal/mole.
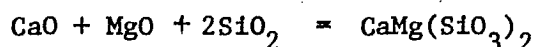
(3) Heat of Mixing

When two or more liquids are mixed, it is very seldom that the physical properties of the mixture are weighted averages of the physical properties of the original components. Even if there is no chemical reaction between the components, the mixing is usually accompanied by some generation or absorption of heat. Therefore, if a substance used in the production of glass is a mixture, the heat which either evolved or had to be supplied at the time when the mixture was formed should be taken into consideration during the fusion of glass.

Neuvonen[6] evaluated the heat of mixing* from the heat-of-solution data for diopside and its components. His value is: $\Delta H = -35,250$ cal/mole.

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*Actually, Neuvonen erroneously named this quantity of heat as "heat of formation". The method that he employed consisted of establishing the heat of solution of each component in hydrofluoric acid at ambient temperature. Then using the relation:

$$\Delta H_{CaO} + \Delta H_{MgO} + 2\Delta H_{SiO_2} - \Delta H_{CaMg(SiO_3)_2} = \Delta H$$

he obtained the value of -35,250 cal/mole. This quantity is in fact the heat of mixing (at ambient temperature) for the reaction:

$$CaO + MgO + 2SiO_2 = CaMg(SiO_3)_2$$

The heat of formation of diopside can be obtained by summing the heats of formation of CaO, MgO and $2SiO_2$ and adding to this sum the above quantity for the heat of mixing. Using Perry's[4] data for CaO, MgO and SiO_2, the heat of formation of diopside adds up to: $\Delta H_f^o = 737,000$ cal/mole.

The difference between the heat requirement of a glass melt and that of one in which $CaCO_3$, $MgCO_3$ and SiO_2 are replaced with a stoichiometric amount of diopside can now be deduced from the above three quantities of heat. Clearly, the sum of (1) and (2) represents a positive value because this is the heat that must be supplied to the original compounds, whereas (3) is a negative quantity, which means that at the time the diopside was formed 35,200 cal/mole were evolved and are hence unavailable in subsequent melting. The latter quantity then must be subtracted from the sum of (1) and (2) when diopside is used. Therefore, (1) + (2) - (3) = 51,816 + 32,016 - 35,250 = 48,582 cal/mole. This is equivalent to 404.4 Btu/lb or 808,800 Btu/ton of diopside.

DISCUSSION AND CONCLUSION

Although a reduction in heat requirement of 808,800 Btu per ton of diopside substituted stoichiometrically for $CaCO_3$, $MgCO_3$ and SiO_2 is an appreciable quantity, the proper perspective can be obtained only by establishing the proportion of the glass mix that can be replaced by diopside and then by comparing the heat saving thus obtained with the over-all heat requirement. Among the numerous types of glass, it appears that glass fiber would be the most suitable. A typical analysis of a glass-fiber batch is (in per cent): 52.8 SiO_2, 8.0 R_2O_3, 20.6 CaO, 7.2 MgO, 9.1 Na_2O, 1.5 K_2O, and 0.8 B_2O_3. The limiting substance in this case is the MgO content, restricting the amount of diopside to a maximum of 38.7%. Leone[7] reports that about 6.25 million Btu are required to produce 1 ton of container glass. Assuming the same requirement for glass fiber, the substitution of diopside will save:

$$100(808,800 \times 0.387)/6.25 \times 10^6 = 5.0\%$$ of the amount of heat required for

production of 1 ton of glass.

This saving of energy, although not large, can be obtained with no alteration to an existing facility. Also, further benefits might be derived from the substitution with diopside. For example, because diopside does not contain carbonates, the decrease of the number of CO_2 bubbles in the glass melt will be proportional to the amount of diopside that can be used as a substitute. Also, it should be noted that the melting point of diopside ($1395^{\circ}C$) is appreciably lower than that of SiO_2 ($1670^{\circ}C$), CaO ($2570^{\circ}C$), and MgO ($2800^{\circ}C$), a fact which might promote faster melting of the glass mix. Finally, transportation and handling of diopside requires less energy: for each 1000 lb mixture of $CaCO_3$, $MgCO_3$ and $2SiO_2$, only 711 lb of diopside are required.

In conclusion, diopside, if available in a sufficiently pure form, will, when used in production of any glass, contribute to lowering the consumption of energy.

ACKNOWLEDGEMENT

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