EFFECT OF TEMPERATURE ON THE HYDRATION OF ORDINARY PORTLAND CEMENT AND THE POZZOLANIC REACTION OF VOLCANIC GLASS POWDER

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ABSTRACT: Volcanic glass powder can be used as a pozzolanic material. Unlike fly ash from industrial waste, it is a sustainable material from volcanic activities. With the publication of JIS A 6209 "Volcanic glass powder for use in concrete", volcanic glass powder started to be used in construction industry. Hydration process of individual cement clinker of ordinary Portland cement and pozzolanic reaction of volcanic glass powder were studied in this research. The water to binder ratio is constant at 0.4 and other parameters of the present study are volcanic glass powder replacement ratio (0%, 10%, 20%), and curing temperature (20, 40, 60°C). XRD/Rietveld analysis and Thermogravimetric analysis were used to obtain the degree of hydration. Selective dissolution method was performed to get the degree of reaction of volcanic glass powder. The pozzolanic reaction of volcanic glass powder was clarified by the difference in the measured portlandite amount and estimated portlandite amount. On the basis of the experimental results, the effect of temperature and volcanic glass powder replacement ratio on the hydration of individual clinker was evaluated. Volcanic glass powder showed high reactivity in the present study. A model of volcanic glass powder reaction rate was proposed based on the model of hydration made by Parrot.

KEYWORDS: Ordinary Portland cement, Volcanic glass powder, Hydration, Pozzolanic reaction, Temperature

1. INTRODUCTION
The hydration of cement is sensitive to the temperature3, higher temperatures lead initially to rapid hydration of each cement clinker but C3A and C4AF have a stagnation at a later age in high temperature environments2. And the hydration of C5S was related to the hydration of C3S but not to the temperature, which was reported in the previous study3.

Volcanic glass powder manufactured from volcanic deposit which is a natural material from volcanic activity. Volcanic ash used in concrete was pointed out as the problem of low workability and slow strength development. However, this problem had been resolved through the dry gravity classification and pulverization by a separating machine and crushing machine, the amorphous content of sorted high-purity volcanic glass particles can increase to 88%, compared to 60% for raw volcanic deposits. The hardened volcanic glass powder--cement mixture has a good performance of compressive strength4, 5. However, the effect of the replacement by volcanic glass powder on the hydration of cement and the pozzolanic reaction of volcanic glass powder at different temperatures are still unclear.

The degrees of reaction of individual clinker and volcanic glass powder were measured by XRD/Rietveld analysis, TG–DTA analysis, and selective dissolution method. The pozzolanic reaction of volcanic glass powder was evaluated by the relationship between reacted volcanic glass powder and consumed portlandite. A model of reaction of volcanic glass powder were proposed based on the experimental results.

2. EXPERIMENTAL PROGRAMS
2.1 Materials and mixing
The ordinary Portland cement (marked OPC) and type II volcanic glass powder (marked VGP) were used. The properties were shown in Table 1 and Table 2. The mineral composition was listed in Table 3. VGP replaces OPC.
Table 1 Properties of OPC

<table>
<thead>
<tr>
<th>Type</th>
<th>ig. loss (%)</th>
<th>Chemical content (mass%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OPC</td>
<td>1.9</td>
<td>SiO₂</td>
</tr>
<tr>
<td></td>
<td></td>
<td>20.68</td>
</tr>
</tbody>
</table>

Table 2 Properties of VGP

<table>
<thead>
<tr>
<th>Type</th>
<th>Chemical content (mass%)</th>
<th>ig. loss (%)</th>
<th>Density (g/cm³)</th>
<th>BET–surface area (cm²/g)</th>
<th>Average particle size (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>VGP</td>
<td>SiO₂</td>
<td>TiO₂</td>
<td>Al₂O₃</td>
<td>Fe₂O₃</td>
<td>MnO</td>
</tr>
<tr>
<td></td>
<td>73.8</td>
<td>0.20</td>
<td>12.5</td>
<td>1.86</td>
<td>0.05</td>
</tr>
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</table>

Table 3 Mineral composition of OPC and VGP

<table>
<thead>
<tr>
<th>Type</th>
<th>Mineral composition (mass%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>OPC</td>
<td>C₃S</td>
</tr>
<tr>
<td></td>
<td>64.29±1.1</td>
</tr>
<tr>
<td>VGP</td>
<td>Quartz</td>
</tr>
<tr>
<td></td>
<td>1.94±0.1</td>
</tr>
</tbody>
</table>

Table 4 Quantified minerals

<table>
<thead>
<tr>
<th>Min</th>
<th>C₃S</th>
<th>C₂S</th>
<th>C₃A</th>
<th>C₆AF</th>
<th>Gypsum</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₃S (Alite)</td>
<td>C₂S (Belite)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₃A (Aluminate phase)</td>
<td>C₆AF (Ferrite phase)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CaSO₄·2H₂O (Gypsum)</td>
<td>CaSO₄·1/2H₂O (Bassanite)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CaSO₄ (Anhydrite)</td>
<td>CaCO₃ (Calcite)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AFm (Monosulphate)</td>
<td>AFm (0.5C)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AFm (C)</td>
<td>AF (Ettringite)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hg (Hydrogarnet)</td>
<td>CHI (Portlandite)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiO₂ (Quartz)</td>
<td>Fe₂O₃ (Magnetcite)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaSiO₄ (Albite)</td>
<td></td>
<td></td>
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<td></td>
<td></td>
</tr>
</tbody>
</table>

At 0%, 10%, and 20% (denoted as VGP0, VGP10, VGP20, respectively) by weight. The water to binder ratio was constant at 0.4.

A twister vacuum mixer made in Germany (Twister II Nr. 1826) was used, with a set speed of 300rpm and a mixing for 5 minutes. The paste was cast into 20×20×20mm cube–shape mould and removed from the mould after 1 day. The samples were cured underwater at a temperature of 20±1°C, 40±1°C, 60±1°C, respectively.

2.2 Compressive strength test

The compressive strength was conducted by the 250kN Autograph made by Shimazu Corporation. According to the JIS A 1108, the loading speed was set as 0.6N/mm²/s. The specimens were fixed by 20mm jig to make the pressure stable.

2.3 XRD/Rietveld analysis

The hydration was stopped by solvent exchange. The samples were crushed into a diameter of less than 5mm debris with a hammer and soaked in isopropanol for 24 hours. The isopropanol was removed by an aspirator pump for 30 minutes. After that, the samples were placed at 11% RH 20±1°C condition until the weight was stabilized.

After drying at 11%RH, the samples were graded with a 75µm sieve, and only the powder passing the sieve was used for the XRD experiment. The XRD experiment was conducted to identify the phase compositions using a RIGAKU Mini Flex diffractometer under the following conditions: Cu–Kα X-ray source, 40kV tube voltage, 15mA tube current, 2θ=5–70° scanning range, 0.02° step width, and 2°/min scanning speed.

Rietveld analysis was performed by TOPAS ver. 6.0. The minerals shown in Table 4 and α–Al₂O₃ (Corundum) admixed with 10wt% as the internal standard were chosen to be quantified. The amorphous phase was calculated from the quantitative value of the corundum according to Eq.[1].

\[
A = \frac{|100 \times (S_R - S)|}{|S_R \times (100 - S)/100|} \quad [1]
\]

Where \(A\) : amorphous material mass
\(S\) : α–Al₂O₃ mixing ratio (%)
\(S_R\) : the quantitative value of α–Al₂O₃ (%)

The degree of hydration and phase composition were assessed by converting all components into anhydrous matter by using the chemical composition and the chemically bound water. The values of chemical composition and chemically bound water referred to the previous study[3]. And the density of each component was assumed to be constant.

2.4 TG-DTA

The powder that stopped hydration was analyzed using a Bruker TG-DTA–MTC–1000SA to quantify changes in the amount of portlandlite. Approximately 40mg of powder was placed in a platinum crucible. The weight was mori-
tored while the powder was heated from 25°C to 1000°C at 10°C/min in a nitrogen atmosphere flowing at 100cm²/min.

The weight loss of portlandite (CH) was determined from the weight loss at 410~485°C with the DTG curve. And through all ignition weight loss (Ig.loss), calculate the amount of bound and absorbed water.

2.5 Selective dissolution method

The degree of reaction of VGP was determined by the selective dissolution method, referred to Asaga et al.\(^6\). The component including the Ca ion was dissolved by HCl solution. The SiO\(_2\), Al\(_2\)O\(_3\) and Fe\(_2\)O\(_3\) gel were dissolved by 5wt% Na\(_2\)CO\(_3\) solution. Finally, only unreacted VGP was left. The samples were handled in the same way as XRD/Rietveld analysis.

The samples (1g) were added to centrifuge tubes containing aqueous HCl (2N, 30mL). And the tubes were placed in a water bath at 60°C for 15min. The solution was stirred with a glass rod every 2min. The samples were separated by centrifugation, and then the samples were washed with hot water (90°C) 3 times. Afterwards the tubes containing the sample were filled with aqueous Na\(_2\)CO\(_3\) (5wt%, 30mL) and placed in a water bath at 80°C for 20min with stirring solution by a glass rod every 2min. The samples were separated by centrifugation and then washed with hot water (90°C) 3times. The residue was dried at 105°C for 24hours. The reaction degree of VGP was calculated from Eq.[2].

\[
D = \frac{k - [R_e \times (1 - Ig_e)] - [R_i \times (1 - Ig_i)]}{R_i \times 100} / h
\]

Where \(D\) : reaction degree of VGP (\(^\circ\))
\(k\) : replacement ratio of VGP (\(^\circ\))
\(R_e\) : residue of sample containing VGP (g)
\(m_e\) : mass of sample containing VGP (g)
\(Ig_e\) : Ig.loss of sample containing VGP (\(^\circ\))
\(R_i\) : residue of sample without VGP (g)
\(m_i\) : mass of sample without VGP (g)
\(Ig_i\) : Ig.loss of sample without VGP (\(^\circ\))

The maturity method is a technique to account for the combined effects of time and temperature on the strength development of concrete\(^7\). This method provides a simple approach for making reliable estimates of in-place strength during construction. The estimate is calculated by Eq.[3].

\[
S = \frac{S_{91} \times (t - S_{91})}{[a + b \times (t - S_{91})]} / h
\]

Where \(S\) : estimate of compressive strength (Mpa)
\(t\) : curing time (days)
\(S_{91}\) : the start of strength development (days)
\(a, b\) : coefficients of time (\(^\circ\))
\(S_{91}\) : compressive strength at 91 days (MPa)
\(h\) : coefficient of \(t - S_{91}\)

The ultimate strengths are different due to the different curing temperatures, but they were ignored here. The ultimate strength was replaced with the strength at 20°C for 91 days.

The “activation energy” was used to assess the effect of temperature. The curing time was converted to the equivalent age by the Eq.[4] referred to the Arrhenius equation.

\[
t_e = \sum_0^t \frac{E}{R \times (T - T_e)} \times \Delta t
\]

Where \(t_e\) : the equivalent age (days)
\(E\) : activation energy (J/mol)
\(R\) : universal gas constant
\(T\) : average temperature during \(\Delta t\) (K)
\(T_e\) : reference temperature (293K)

Because the curing at high temperature started after the demolding, \(T = 293K\) when \(t = 1\).

Fig. 1, Fig. 2, Fig. 3 showed the experimental results and the fitting curve. Based on these fitting curves, the apparent activation energy of each mixture was obtained as 20kJ/mol for VGP0, 25kJ/mol for VGP10, and 30kJ/mol for VGP20, respectively. Based on this result, the apparent activation energy of the VGP-cement mixture was higher than that of plain cement. The equivalent age increased faster with the increase of apparent activation energy. It is suggested that the reaction of VGP contributes more efficiently to the development of compressive strength than that of the ordinary Portlandite cement.

3. EXPERIMENTAL RESULTS

3.1 Compressive strength

The compressive strength was tested with the samples at curing times of 1, 3, 7, 28 and 91days. The maturity method was used to estimate the compressive strength development.

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3.2 The results of XRD/Rietveld analysis

Fig. 4 shows the results of XRD/Rietveld analysis. The VGP accelerated the initial hydration of cement clinker at 20°C. It can be considered that it is because the filling ef-
fert of VGP increased the effective water to cement ratio and provided the additional nucleation sites for hydrates from the OPC. This filling effect of VGP became smaller from the age of 7 days at 20°C in Fig. 4, which is the same as fly ash. In addition, when the curing temperature increased, the filling effect by VGP decreased. It can be confirmed from Fig. 4, 40°C and 60°C. Increased temperature promotes the hydration of cement clinker at an early age. However, the impact of temperature on the hydration was different for individual clinker.

Fig. 5 organized the results of XRD/Rietveld analysis and shows the relationship between the hydration degree of C₃S and C₃S at the same curing time. The light orange line corresponds to VGP0, the dark red line to VGP10, the red line to VGP20. The hydration of C₃S was reactivated with the hydration degree of C₃S. It has been proved that the relationship is not related to the water to cement ratio and temperature. The hydration of C₃S is related to the solubility of C₃S. When the cement and water start to contact, because of the dissolution of C₃S, the liquid phase rapidly saturates with CaO/SiO₂ = 3. The C₃S is hard to dissolve due to the concentration of CaO and SiO₂ is too high. With the hydration of C₃S coming to an end, the dissolution and hydration of C₃S become fast. It can also be confirmed from Fig. 4. However, the parameters changed by the VGP replacement ratio, and the correlation factor decreased as shown in Fig. 5.

The stagnation of hydration of C₃A and C₃AF was confirmed in Fig. 4, 40°C and 60°C. This was caused by the formation of gel hydrate on the surface of C₃A and C₃AF. The gel hydrate is amorphous including sulfate ions and carbonate ions. It can be considered that more gel hydrate was generated at 40°C and 60°C. The gel hydrate densification on the surface of C₃A and C₃AF hinders ion transfer, and hydration is stalled. On the other hand, the VGP reduced the effect of stagnation on the hydration of C₃A and C₃AF compared with plain OPC. With the increasing of VGP replacement ratio, the hydration degree of C₃A increased at 40°C and 60°C. The hydration of C₃AF at 40°C and 60°C was almost independent of VGP, but comparison with VGP0 showed an increasing trend of hydration. It can be considered that the amount of the gel hydrate decreased because the proportion of cement decreased due to the replacement by VGP. Therefore, the densification of the gel hydrate was weakened, and hence the blocking effect of ion movement decreased.

3.3 Degree of reaction of VGP

The degree of reaction of VGP was evaluated by the selective dissolution method and the results were presented in Fig. 4. Although the rate of reaction of VGP was slow at 20°C, both the degree of reaction of VGP of VGP10 or VGP20 was over than 10% at an age of 28 days. The VGP used in the present study showed a higher degree of reaction than the reported values of Japanese fly ash at 20°C. In addition, the reaction of VGP was influenced strongly by the temperature.

4. DISCUSSION

4.1 Hydration analysis

The hydration of cements can be assumed to take place via dissolution and precipitation processes. The approach of Parrot and Killah was applied to reproduce
the hydration rate. The hydration of the individual clinker phases was described by three equations Eq.[5], Eq.[6], and Eq.[7], where the lowest value among them at time t was the rate-controlling step. The degree of hydration $\alpha$ at time $t$ is expressed as Eq.[8]. The effect of temperature on the hydration rate was expressed by the Eq.[9] which referred to the Arrhenius equation.

$$R_i = \frac{K_i}{N_i} (1 - \alpha_i) \left(- \ln (1 - \alpha_i) \right)^{(1 - N_i)}$$  [5]

$$R_i = \frac{K_2 \times (1 - \alpha_i)^{T}}{1 - (1 - \alpha_i)^{T}}$$  [6]

$$R_i = K_3 \times (1 - \alpha_i)^{N_i}$$  [7]

$$\alpha_i = \alpha_{i-1} + \Delta t \cdot R_i$$  [8]

$$R_{t, T} = R_{t, T_0} \cdot e^{\frac{E}{RT} \left(\frac{1}{T} - \frac{1}{T_0}\right)}$$  [9]

Where $R_i$: hydration rate of each clinker at time $t$ (-)

$K_i$, $N_i$, $K_2$, $K_3$, $N_i$: constants of hydration of individual clinker (-)

$\alpha_i$: degree of hydration (-)

$E$: activation energy (J/mol)

$R$: universal gas constant

$T$: curing temperature (K)

$T_0$: reference temperature (293K)
The effect of water binder ratio was not considered in this model. This is because it has been proved that the effect of water binder ratio on the hydration rate is very small\(^5\). In addition, all samples were cured underwater, which means the water is sufficient for the hydration of cement.

The apparent activation energies were given in Table 5. The reported activation energy from previous studies were reviewed. It can be confirmed that the apparent activation energies of C\(_2\)S and C\(_3\)S are very high in the cement system, which means the effect of temperature on C\(_2\)S and C\(_3\)S is high. The apparent activation energy of C\(_2\)A and C\(_4\)AF is lower than previous studies due to the stagnation of hydration.

With the addition of VGP, the apparent activation energies of all clinkers in cement were decreased. The higher the VGP replacement ratio, the lower the apparent activation energies.

4.2 Pozzolanic reaction of VGP

The pozzolanic reaction of VGP was discussed by evaluating the amount of portlandite. The portlandite content was quantified by XRD/Rietveld analysis. The development of portlandite is presented in Fig. 6. The curves of “VGP0 Portlandite” and “Measured” are the measured values. The curves of “VGP0×0.9” and “VGP0×0.8” are the measured value of VGP0 multiplied by the corresponding percentage of cement mass. The curve of “Prediction—cement base” is the predicted value by the reaction of C\(_2\)S. It was assumed that consumption of 1mol C\(_2\)S produced 1mol portlandite.

The filling effect of VGP can also be confirmed by the difference between “Prediction cement base–20°C” and VGP0×0.9(0.8)–20°C” in Fig. 6. More portlandite was produced because of the filling effect of VGP. The higher the replacement ratio, the higher the filling effect.

The consumed portlandite of pozzolanic reaction was calculated by the comparison of “Prediction cement base” and “Measured”. The consumption of portlandite of 20°C was very small, and the consumption of portlandite of 40°C and 60°C increased rapidly. This result is the same as discussed in 3.3.

Based on the degree of reaction of VGP and the consumed portlandite, an empirical formula was given in Fig. 7. The relationship between the reacted glass and consumed portlandite is definite and does not change with the replacement ratio and the temperature. 0.7g of portlandite is consumed for every 1g glass reacted.

The chemical reaction equation Eq.[10] of VGP was given. Only the glass phase in the VGP was considered as the reactant. The chemical content of the glass was performed by Al\(_2\)O\(_3\) and SiO\(_2\). The mass ratio of Al\(_2\)O\(_3\) and SiO\(_2\) was used from Table 2.

### Table 5 Activation energy of individual clinker

<table>
<thead>
<tr>
<th>Phase</th>
<th>E (kJ/mol)</th>
<th>System</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(_2)S</td>
<td>455</td>
<td>42(^1), 58(^2), 26(^3)</td>
</tr>
<tr>
<td>C(_3)S</td>
<td>60</td>
<td>21(^1), 58(^2), 96(^3)</td>
</tr>
<tr>
<td>C(_2)A</td>
<td>24</td>
<td>54(^1), 72(^2)</td>
</tr>
<tr>
<td>C(_4)AF</td>
<td>24</td>
<td>34(^1), 72(^2)</td>
</tr>
<tr>
<td>C(_2)S</td>
<td>45, 30</td>
<td>VGP–OPC mixture</td>
</tr>
<tr>
<td>C(_3)S</td>
<td>60, 40</td>
<td></td>
</tr>
<tr>
<td>C(_2)A</td>
<td>20, 15</td>
<td></td>
</tr>
<tr>
<td>C(_4)AF</td>
<td>25, 10</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\), \(^b\), \(^c\) Used apparent activation energy in the present study. \(^b\), VGP0, \(^c\), VGP10, \(^b\), VGP20

![Fig. 6 Development of portlandite with time](image-url)
The generates from the reaction of VGP was assumed as C–A–S–H, the same as supplementary cementitious materials, but the Ca/(Si + Al) ratio and bound water were not evaluated in the present study.

\[ S + 0.1A + 0.7CH + xH \rightarrow C–A–S–H \]  \[ 10 \]

Where \( S \) is SiO\(_2\), \( A \) is Al\(_2\)O\(_3\), \( CH \) is Ca(OH)\(_2\), and \( H \) is H\(_2\)O.

4.3 Model of VGP reaction rate

A simple model of VGP reaction rate was given through the above data analysis. The equation Eq.[11] was derived using the hydration model of Parrot and Killoh as a prototype and considering the effect of the fineness and the VGP replacement ratio.

\[ R_t = F \times S \times P \times (1 - a)_t \]  \[ 11 \]

Where \( R_t \) : reaction rate of VGP at time \( t \) (\( \cdot \))

\( F \) : effect of fineness (\( \cdot \))

\( S \) : effect of VGP replacement ratio (\( \cdot \))

\( P, L \) : constants of VGP reaction rate (\( \cdot \))

\( F = 69000/3300, 3300 \) is a reference fineness. The effect of temperature was evaluated by the Eq.[9] with the apparent activation energy. The parameters were given in Table 6.

The apparent activation energy of VGP in the present study was higher than that of individual clinker of cement by the comparison of Table 5 and Table 6.

Fig. 8 showed the comparison of the predicted value and measured value. It can be confirmed the model of VGP reaction rate is reasonable. Fig. 9 showed the details.

### Table 6 Parameters of model of VGP reaction

<table>
<thead>
<tr>
<th>VGP</th>
<th>0.01</th>
<th>0.008</th>
<th>6.0</th>
<th>75</th>
</tr>
</thead>
<tbody>
<tr>
<td>VGP20</td>
<td>0.005</td>
<td></td>
<td></td>
<td>80</td>
</tr>
</tbody>
</table>

By comparing the reaction rates of VGP at different temperatures, the pozzolanic reaction of VGP is influenced by temperature strongly. The reaction rate of VGP increased with the temperature.

5. CONCLUSION

The hydration of ordinary Portland cement and the pozzolanic reaction of volcanic glass powder was investigated based on XRD/Rietveld analysis, thermogravimetric analysis, and selective dissolution method.

Followings are the summary of the obtained experimental results:

![Fig. 7 Relationship between the reacted glass and the consumed portlandite](image)

![Fig. 8 Comparison of the predicted value and measured value](image)

![Fig. 9 Comparison of calculated reaction degree of VGP as a function of time and temperature with the results of selective dissolution method](image)
1. The development of the compressive strength of a given VGP–OPC mixture at different temperatures can be estimated by the maturity method. The apparent activation energy of VGP0 is 20kJ/mol, VGP10 is 23kJ/mol, and VGP20 is 30kJ/mol, respectively.

2. When temperature changes or VGP is mixed with OPC, the hydration rate of individual clinker is affected. The apparent activation energy of individual clinker decreases with the increase of VGP replacement ratio.

3. The pozzolanic reaction of VGP was clarified in the VGP–OPC system and an empirical formula was proposed for the pozzolanic reaction of VGP. VGP reacts with portlandite in a ratio of 1g to 0.7g.

4. Based on the experimental results and the model of hydration rate, a model of VGP reaction rate was established and used to evaluate the apparent activation energy of VGP. VGP has a high apparent activation energy in the VGP–OPC system. When the VGP replacement ratio is 10%, the apparent activation energy is 75kJ/mol, and when the VGP replacement ratio is 20%, it is 80kJ/mol.

REFERENCES:


