

ZERO EMISSIONS POWER GENERATION WITH CO₂ REDUCTION BY FAYALITE

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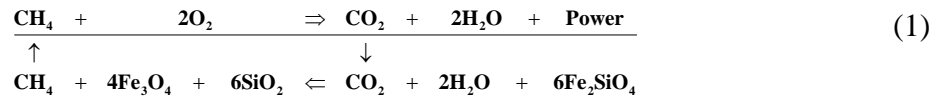
Abstract

In this paper a new ‘fuel’, fayalite Fe₂SiO₄, is proposed tentatively and a new concept involving the convergence of a power plant and its fuel source is described. The CO₂ from the power plant would be injected underground where it would be reduced to methane. The methane would then serve as the ‘derived fuel’ of the power plant having been produced by the reaction of fayalite with the CO₂. One of the possible chemical reactions of CO₂ with rock is indicated, along with properties of the mineral fayalite. Calculations of the Gibbs free energy and enthalpy show that the reaction of carbon dioxide with fayalite is exothermic and might be self-sustaining.

The concept

The concept, which was first described by Yantovski¹ with some reactions from the literature, is attractive because any stream of carbon dioxide that was to be sequestered could be used for new fuel production in an artificial geochemical reactor, rather than simply being stored underground.

Let us consider the simplified chemistry of carbon reactions, Equation 1, in a zero emissions power plant (above the line) and in an artificial geochemical reactor deep underground (below the line).



The four arrows clearly show the closed cycle of carbon, which plays the role of an energy carrier from fayalite to methane and then to the power plant. At quite realistic conditions of some hundreds of degrees Celsius and some hundreds of bar the reaction is exothermic and may be self-sustaining.

The thermal energy of reaction between high-pressure supercritical carbon dioxide with water and fayalite is enough to heat the reaction products up to 250°C. However, the question of the conversion time is still open. In other words, what are the kinetics of reaction? An experiment in a *P-V-T* calorimeter should answer this question.

The reaction mentioned above is not unique. There have been somewhat similar experiments involving the production of abiogenic methane².

Fayalite as a tentative ‘fuel’

Having looked at the above reactions, one might view carbon as having a role as a carrier of energy, whereas the major role would be played by the tentative ‘fuel’, fayalite, Fe₂SiO₄, which is sometimes expressed as (FeO)₂SiO₂. This well-known mineral is called after the Portuguese island of Fayal.

Fayalite consists of the most abundant elements within the Earth: oxygen, silicon and iron. It could be synthesised from some industrial processes. In smelting processes for nickel and steel production the slag contains fayalite.

The amount of fayalite in the Earth’s crust is tremendous. It may well have the potential to allow methane to be considered in the same category as the family of renewable sources of energy in terms of its impact on the environment, particularly in relation to the greenhouse effect. In the USA some major locations of fayalite are Alaska (all), Nevada (Black Mountain, Silent Canyon Volcanic Center), Texas (Terlingua-Big Bend), and Vermont (Cuttingsville)³.

Thermodynamics of the reaction

For the reaction



the thermodynamic data from the SUPCRT92 database application⁴ are used. Details are given in Table 1. Thermodynamic properties of both liquid and/or gaseous H₂O were calculated using Hill's equation of state⁵. As a result for the reaction, Equation 2, at 250°C and 200 bar we have:

Table 1

Substance	Enthalpy, <i>h</i>	Enthalpy, <i>h</i>	Gibbs free energy, <i>g</i>	Gibbs free energy, <i>g</i>
	cal/mol	J/mol	cal/mol	J/mol
Fayalite	-345785	-1446764	-340386	-1424175
H ₂ O	-64091	-268156	-61605	-257755
CO _{2,gas}	-91776	-383990	-106419	-445257
Magnetite	-257662	-1078057	-251712	-1053163
Quartz	-214651	-898100	-207596	-868582
CH _{4,gas}	-15618	-65345	-22794	-95370

So, for the reaction

$$\begin{aligned} \Delta_r G_{250^\circ, 200 \text{ bar}} &= 4(-1053163) + 6(-868582) + (-95370) - 6(-1424175) \\ &\quad - 2(-257755) - (-445257) = -14097 \text{ J} \end{aligned}$$

$$\begin{aligned} \Delta_r H_{250^\circ, 200 \text{ bar}} &= 4(-1078057) + 6(-898100) + (-65345) - 6(-1446764) \\ &\quad - 2(-268156) - (-383990) = -165287 \text{ J} \end{aligned}$$

The last value means that the reaction is exothermic.

The decimal logarithm of the thermodynamic constant of reaction for Equation 2 is

$$\lg K_a = \lg \frac{f_{CH_4}}{f_{CO_2}} = -\frac{\Delta_r G}{2.303RT} = -\frac{-14097}{2.303 \times 8.314 \times 523.15} = 1.41$$

Use of Redlich-Kwong equation of state shows that the fugacity coefficients of the gases are close to 1 ($\gamma_{CO_2} = 0.87$, $\gamma_{CH_4} = 1.01$ at the T and P specified). This means that

$$\lg K_a = 1.41 \approx \lg \frac{P_{CH_4}}{P_{CO_2}},$$

thus

$$\frac{P_{CH_4}}{P_{CO_2}} = 25.6.$$

The last value brings the conversion factor of CO_2 into CH_4 close to 96%.

Forthcoming experiments

We are not aware of any experiments that have been done on the interaction of fayalite and carbon dioxide. But a similar reaction in an autoclave with comminuted (37 - 106 micrometers) forsterite Mg_2SiO_4 was extensively examined in the Albany Research Centre⁶. The chemical energy of the forsterite is 256.8 kJ/mol. The reaction products are magnesite $MgCO_3$ and silica or silicic acid. The pressure was 117 - 127 atm and temperature 185 - 188°C. The test time spans were from 3 to 48 h. It was observed that there was a large increase of the reaction rate when carbon dioxide was in a supercritical state.

Similar experiments with comminuted fayalite might shed light on the kinetics and applicability of the reaction for methane production. Experiments should be carried out ex-situ at first, then in-situ. For in-situ experiments the formation of cracks, as done in the recovery of geothermal energy from hot dry rock, might be useful.

Conclusion

Calculations show that the reaction between fayalite and CO₂ is exothermic and might be self-sustaining. The next step should be an experimental demonstration of the reaction of comminuted fayalite with carbon dioxide and water at conditions such as those mentioned in the paper. It is also possible that some better 'fuels' than fayalite might be discovered.

References

1. Yantovski E. On the geochemical hydrocarbon reactor concept. Fifth Intern. Conf. On Carbon Dioxide Utilization, Sept. 5-10, 1999, Karlsruhe, P. 51, pp 224-225.
2. Horita J., Berndt M. Abiogenic methane formation and isotopic fractionation under hydrothermal conditions. Science, 1999, v. 285, pp 1055-1057.
3. Wooley A. Alkaline Rocks and Carbonates of the World. p. 1, British Museum (Natural History) London, 1987.
4. Johnson J.W., Oelkers E.H. and Helgeson H.C. SUPCRT92: A software package for calculating the standard molal thermodynamic properties. Comp. Geosci., 1992. V18. pp 899-947.
5. Hill P.G. A unified fundamental equation for the thermodynamic properties of H₂O. J. Phys. Chem. Ref. Data, 1990, 19, pp 1233-1247.
6. O'Connor et al. Carbon dioxide sequestration by ex-situ mineral carbonation. Second Dixy Lee Ray Memorial Symp. 31 Aug. - 2 Sept. 1999, Washington, DC.

Zero Emissions Power Generation with CO₂ Reduction by Fayalite

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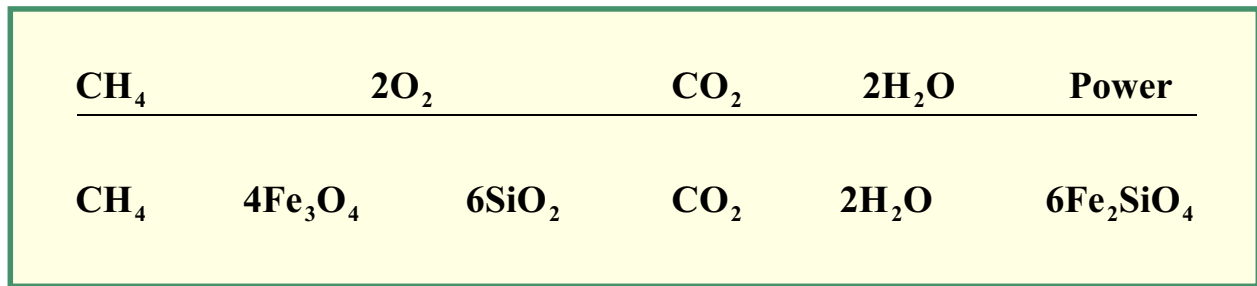
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The concept

- Any stream of carbon dioxide that was to be sequestered could be used for new fuel production.
- An artificial geochemical reactor with a mineral such as fayalite would be used.
- The question of the conversion time is still open. In other words, what are the kinetics of reaction?



Fayalite as a tentative 'fuel'

- Carbon would have a role as a carrier of energy, whereas the major role would be played by the tentative 'fuel', fayalite, Fe₂SiO₄.
- Fayalite consists of the most abundant elements within the Earth: oxygen, silicon and iron.
- In the USA some major locations of fayalite are Alaska (all), Nevada (Black Mountain, Silent Canyon Volcanic Center), Texas (Terlingua-Big Bend), and Vermont (Cuttingsville).

Forthcoming Experiments

- Experiments with comminuted fayalite might shed light on the kinetics and applicability of the reaction for methane production.
- Experiments should be carried out ex-situ at first, then in situ.
- For in-situ experiments the formation of cracks, as done in the recovery of geothermal energy from hot dry rock, might be useful.

Conclusion

- Calculations show that the reaction between fayalite and CO₂ is exothermic and might be self-sustaining.
- The next step should be an experimental demonstration of the reaction of comminuted fayalite with carbon dioxide and water at conditions such as those mentioned in the paper.
- It is also possible that some better 'fuels' than fayalite might be discovered.

Presenter

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