

Heat as by-product or sub-product of CO₂ storage in mafic and ultramafic rocks

Diogo Rosa¹, Rui Rosa²

Abstract — Since carbonates are at a lower energy state than free CO₂, storage through carbonation of silicate rocks is thermodynamically favoured and proceeds spontaneously by releasing heat. In an in-situ CO₂ injection site, the heat released in these exothermic reactions can be exploited in a geothermal plant, effectively contributing towards the economic viability of the storage process.

Our calculations suggest the possibility of generating up to about 65 TWh of electrical energy while capturing permanently about 1Gton CO₂ per 1 km³ of peridotite or basalt rock. That broadly corresponds to exploring an electric power plant having up to 150 MW gross output during a period of 50 years.

These results show that geothermal energy and CO₂ storage, often portrayed as conflicting uses of the subsurface, can actually work together, enhancing the economic feasibility of each other in case mafic and/or ultramafic rock formations are used as reservoirs.

Keywords — basalt, carbonation, CO₂ storage, geothermal heat

1 INTRODUCTION

Mafic and/or ultramafic rocks have been proposed as a potential CO₂ storage solution, along with saline aquifers, depleted hydrocarbon reservoirs and coal seams. In addition to their widespread geographic distribution, mafic and/or ultramafic rock formations have a favourable mineralogy and chemistry which allows for the conversion of CO₂ to a carbonate mineral phase, effectively removing the greenhouse gas permanently from the atmosphere. This carbonation reaction can take place in-situ, if CO₂ is injected in a suitable geological reservoir, or using mined waste-rock. The inherent stability of the carbonate mineral phase will certainly contribute towards the social acceptance of CO₂ storage and therefore basalt and/or ultramafic rock formations merit further research as a CO₂ storage solution.

The favourable mineralogy for carbonation includes olivines (fayalite and/or forsterite), serpentines and, to a certain degree, pyroxenes (diopside, hypersthene and/or augite) and plagioclases (namely anorthite). Olivines dominate in peridotite and their hydrated counterpart serpentines dominate in serpentinite, both ultramafic rocks types that can also contain pyroxenes. Mafic rocks, such as basalts and gabbros, on the other hand, also have olivine but pyroxenes and plagioclases dominate.

Carbonation reactions of these minerals display negative reaction changes of both Gibbs free energy and of enthalpy. That means that mineral constituents of such rocks in the presence of CO₂ tend to spontaneously evolve into carbonates and

free silica, releasing thermal energy in the process [1], [2], [3].

These reactions, however, display negative reaction changes of entropy and positive reaction changes of volume of the solid phase. These are thermodynamic unwelcome properties, because they imply that, for the relevant mineral constituents, rising either temperature or overall pressure will reduce the free energy that drives the reaction in the positive sense. This means that carbonation will take place but only up to certain maximum temperature and pressure limits. In particular, it cannot take place deep in the crust, where very high temperature and lithostatic pressure will drive the reaction in the opposite sense. This is why in subduction zones decarbonation reactions take place, carbonates being converted to silicates and C is liberated and CO₂ outgassed, at the prevailing very high pressure and temperature. The positive change in volume, from reactants to products, is an unwelcome property also because the reaction products (carbonates and silica) can obstruct the path for further fluid flow, although the generated inter-grain mechanical stresses, under the confined in-situ injection circumstances will assist in furthering the fracture and fissure networks in the rock matrix and mineral grains. The results of these effects will be site specific and have to be addressed in detail, eventually implying regular fracking procedures to enhance permeability and allow for the carbonation reactions to continue. As to the partial pressure of the injected CO₂, its increment will be a valuable tool available to displace the reaction in the positive sense and to accelerate the reaction kinetics, in the light of the mass action law.

1-LNEG - Laboratório Nacional de Energia e Geologia, Alfragide, 2720-866 Amadora, Portugal.

CREMINER, University of Lisbon, 1749-016 Lisboa, Portugal.

2- Emeritus Professor, Physics Department and Geophysics Center, University of Évora, 7000-671 Évora, Portugal.

Summarizing, the in-situ injection of CO₂ in mafic and ultramafic rock formations is promising, not only for the sequestration of CO₂ but also as a means of enhancing the availability and temperature of geothermal heat collection, if rock permeability is not too low, and fluid pressure can be increased and maintained high enough to attain a favourable rate of chemical reaction and consequent heat release rate. The present paper attempts to prove that recovering the heat released in the in situ carbonation process can be carried out with a favourable energy budget, and attempts to suggest approaches to its extraction, which can effectively contribute towards the economic feasibility of CO₂ injection into mafic or ultramafic rocks. The resulting enhanced economics will assist in the safely and permanent disposal, in a geological reservoir, of this greenhouse gas resulting from the combustion of fossil fuels.

2 MAIN ASSUMPTIONS AND RESULTS

Carbon dioxide is well known for its favourable properties as a heat transfer (also mass transfer) agent [4]. In the case under consideration, supercritical CO₂ is envisioned, at up to 1000 bar and 200°C. Supercritical CO₂ displays fairly high heat capacity ($c \approx 1$ kJ/kg.K) and volumic mass ($\rho \approx 0.3$ kg/m³), and rather low kinematic viscosity ($\nu \approx 10^{-7}$ m²/s) and heat diffusivity ($a \approx 10^{-7}$ m²/s); fluid compressible factor $Z = Pv/RT$ stays close to unity [5].

Favourable operation circumstances require a sufficiently large rock mass, so that carbonation reactions take place in a volume of rock of the order of one km³. The relative abundance of ultramafic and, specially, mafic rock formations warrants the existence of numerous locations fulfilling this requirement for CO₂ injection. Such locations will occur in ophiolite complexes in alpine belts and mafic rocks, in addition, also occur in large continental flood basalt provinces as well as large intrusions (Fig. 1).



Fig. 1 - Global distribution of continental flood basalts and ophiolite belts.

Ideally, conditions for fluid trapping between impermeable layers and/or structures such as folds and faults would be an advantage. Otherwise a fluid collection network would be required to re-inject the CO₂. In any case, sufficient rock porosity and

permeability are necessary, so that fluid flow without undue power consumption can be established, and to insure a large specific area for the carbonation reaction to take place at a fair pace. For this, fracking procedures, already common place in the hydrocarbon and geothermal industries, will likely have to be implemented.

Regarding heat generation and confinement, CO₂ should be injected up to a pressure level high enough to induce the carbonation reaction to take place at a fair rate over a volume of rock of the order of $V \approx 1$ km³. The carbonation might last many decades until equilibrium between reactants and products is attained, at the temperature and pressure prevailing in the reservoir. Heat diffusion takes place at a pace such that, in a reservoir with the volume defined above, the heat essentially stays confined in a time scale of one hundred years. As a matter of fact, for:

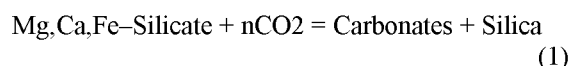
heat diffusivity (a) $\approx 10^{-6}$ m²/s (Table 1),
reservoir diameter (L) $\approx 10^3$ m,
and time (t) $\approx 3.10^9$ s (100 hundred years)

the Fourier number (Fo) = $at/L^2 \approx 0.003 \ll 1$, which means that generated heat will practically not have diffused out of the reservoir volume within that time frame.

Table 1. Properties of some significant rock types [6], [7]

Rock type	Density 10 ³³ .kg/m ³	Porosity 10 ⁻²	Thermal capacity kJ/kg.K	Heat diffusivity 10 ⁻⁷ m ² /s
Peridotite	2.4-3.0	0.3-2.0	0.92-1.09	12.0-14.1
Serpentinite	2.0-2.5	0.8-12	0.96-1.13	
Gabbro	2.5-2.7	0.2-3.0	0.90-1.13	9.3-12.2

Carbonation of silicate minerals and rocks can be synthesized in the formula:



water might be present too as a reactant or a product.

We consider two representative rock types to illustrate and test the concept under scrutiny. One is a peridotite composed by forsterite and fayalite in equal proportion; the other one is a basalt composed by diopside, forsterite and anorthite in equal proportions.

The thermodynamics of the chemical changes are governed by the changes in Gibbs free energy of the substances in presence

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ \quad (2)$$

$$\Delta G^\circ = \sum_n G_n^\circ \quad (3)$$

G_n° standing for the standard Gibbs free energy of formation (J/mol), the sum \sum_n encompassing all of each product (adding) and each reactant (subtracting). Likewise for the standard enthalpy of

formation $\Delta H^\circ = \sum_n H_n^\circ$ (J/mol) and the standard entropy $\Delta S^\circ = \sum_n S_n^\circ$ (J/mol.K).

For not standard conditions, one has:

$$\partial\Delta G/\partial P = \Delta V \quad (4)$$

$$\partial\Delta G/\partial T = -\Delta S \quad (5)$$

The properties of the carbonation reactions of relevant minerals and of the rocks are given in Table 2. These are deduced from the standard state thermodynamic data for those minerals which are available in the literature.

Table 2. Carbonation of some minerals and rocks.

Molar quantities of minerals and rocks: Mass M (g/mol); Heat capacity C (J/mol.K). Molar quantities changes in carbonation reaction (standard conditions): Free energy ΔG° (kJ/mol); Enthalpy ΔH° (kJ/mol); Entropy ΔS° (J/mol.K); Volume ΔV° (10^{-5} m³/mol) [8], [9], [10], [11], [12], [13]

Mineral or Rock Properties	M g	C J/K	ΔG° kJ	ΔH° kJ	ΔS° J/K	ΔV° 10^{-5} m ³
Diopside CaMgSi ₂ O ₆	217	168	-63	-162	-333	2.08
Hypersthene MgFeSi ₂ O ₆	232	169	-33	-135		
Enstatite Mg ₂ Si ₂ O ₆	201	115	-64	-170	-348	3.88
Forsterite Mg ₂ SiO ₄	141	118	-71	-175	-352	3.50
Fayalite Fe ₂ SiO ₄	204	135	-65	-169	-348	3.52
Serpentine Mg ₃ Si ₂ O ₅ (OH) ₄	277		-61	-194		2.24
Anorthite CaAl ₂ Si ₂ O ₈	278	210	-73	-229	-495	3.54
Peridotite	173	125	-68	-172	-350	3.51
Basalt	212	165	-69	-189	-393	3.04

For the two rock types being examined, one has $\Delta G \approx -70$ J/mol of mineral at standard pressure (1 bar) and temperature (298 K) conditions. The carbonation reaction is spontaneous ($\Delta G < 0$) and releases $(-\Delta H) \approx 180$ J/mol as heat. For a given rock mass, the total amount of heat energy that is released until full carbonation is attained, is given by:

$$H = (\rho/M) (-\Delta H) V \quad (6)$$

In our study case, having also $V \approx 1$ km³ and $\rho \approx 2.7$ g/cm³, **H** amounts to ≈ 2.5 EJ (10^{18} J). That amount, if released along a lifespan of 100 years, would correspond to an average thermal power of nearly one GW.

Temperature in the reservoir will rise with the carbonation heat being released and added to the rock, at parallel rates according to the proportion:

$$(-\Delta H) = C \Delta T \quad (7)$$

where C (J/mol.K) stands for the heat capacity per mole of reaction (an average value between the heat capacity of reactants and products).

However, the reaction free energy drop ΔG° diminishes with increasing temperature, according to Eq. (5), given that $\Delta S^\circ < 0$. Consequently, the reaction tends to an equilibrium ($\Delta G = 0$) and the carbonation stops at a temperature lift ΔT (relative to the reference temperature 298 K) given by:

$$\Delta T \approx (-\Delta G^\circ)/(-\Delta S^\circ). \quad (8)$$

The maximum temperature that can be attained is thus estimated at 492 K (219 °C) in the case of the peridotite and 474 K (201 °C) for the basalt under consideration. Higher temperatures can be achieved with some other mineralogical compositions [1].

Similarly, Eq. (4) tells us that the carbonation reaction halts and reverses when the lithostatic pressure (relative to the reference pressure 1 bar = 100 kPa) attains and exceeds:

$$\Delta P \approx (-\Delta G^\circ)/(\Delta V^\circ). \quad (9)$$

The pressure that halts the carbonation is very high, estimated at close to 2 GPa or 20 kbar for both rock types. Therefore, contrasting with the influence of temperature, the influence of depth (for pressure) in the geological reservoir can be neglected in our analysis.

3 PROPOSED APPROACH

Based on the results obtained above, we propose to employ CO₂ as a feedstock in a two step sequestration and geothermal exploration concept. Firstly, as a chemical agent, CO₂ is used to promote the generation of heat by carbonation of silicate mineral constituents of mafic and ultramafic rocks. During this stage CO₂ is basically being sequestered while raising the reservoir's temperature. Secondly, while CO₂ is still being sequestered, CO₂ starts to be also used as a heat transfer fluid, to extract the heat previously generated to be used either directly or for conversion in an electrical power plant.

To achieve this concept, CO₂ in a supercritical state is made to circulate through the rock by means of a set of input (injection) and output (production) wells, implanted in such a way as to drive the fluid to flow and fill the whole reservoir, by convection through the fracture network, and by diffusion into the rock matrix. The permeability of intact not fractured rock is a very important property, in order

to allow for the fluid to diffuse at a fair rate and access the whole rock body.

The operation of the carbonation reaction can be controlled within limits by regulating the partial pressure and the flow rate of the CO₂ within the reservoir; by adding water steam or other additives; by letting the rock temperature rise; by resorting to fracking. For each mineralogical composition a maximum temperature can be attained that achieves the highest carbonation rate and conversion ratio [1], [2], [14].

Once the heat provided by the carbonation reactions, added to the pre-existing regional geothermal heat flow, has brought the rock temperature to the desired level, the operation moves from the first stage to the second stage. This will likely occur after a period of up to a decade. At this stage CO₂ will be made to flow to the effect of collecting and extracting the heat generated, at an acceptable level of power spent in driving the forced circulation. On the other hand, the flow rate should be adjusted to the rate of heat generation from then on, such that the temperature and the collected heat power shall be kept to their long time target levels.

At this stage one should ensure that the power spent in pumping the cooling fluid (supercritical CO₂) is much smaller than the exergy extracted from the wells. We assume that the dissipation resides mostly in the flow through the rock matrix (being comparatively negligible in the down welling and upwelling legs of the cooling circuit). As to the pumping power one has:

$$dW/dt = v Q (P_1 - P_2) \quad (10)$$

v standing for the massic volume and Q for the mass flow rate of the fluid, and (P_1, P_2) for the fluid pressure at the outlet of injection wells and at the inlet of the collecting wells, respectively. With regard to the extracted heat power one has:

$$dH/dt = c Q (T_2 - T_1) \quad (11)$$

where c stands for the fluid heat capacity, and $T_2 - T_1$ for the temperature increment of the fluid from the outlet of the injection wells to the inlet of the collecting wells.

The condition $dW/dt \ll dH/dt$ must be satisfied, that is, by combining Eqs. (10) and (11):

$$(P_1 - P_2) \ll \rho c (T_2 - T_1) \quad (12)$$

where $\rho = 1/v$ is the volumic mass; ρc denotes the volumic heat capacity of the fluid. Full thermal potential is attained when $T_2 \rightarrow T_g$ that is the geothermal rock temperature, and $T_1 \rightarrow T_\infty$ that is the (above ground) environment temperature. More exactly, comparing actual work spent to potential work or exergy collected by the thermal fluid, one must satisfy the criterion:

$$(P_1 - P_2) \ll (1 - T_\infty/T_g) \rho c (T_g - T_\infty) = \rho c (T_g - T_\infty)^2 / T_g \quad (13)$$

$(1 - T_\infty/T_g)$ being the theoretical Carnot efficiency. Eq. (13) supersedes (12).

The upper bound to the difference $(P_1 - P_2)$ increases through (ρc) with the pressure of the fluid (supercritical CO₂) across the reservoir, and through T_g with the rock temperature. At two hundred degree temperature lift, $(T_g - T_\infty) \approx 200$ K, and at least several hundred bar working pressure, $(\rho c) \approx 1000$ kJ/m³.K, the upper bound imposed on the pressure drop attains close to 1000 bar. So that one is allowed to drive the cooling circuit with a pressure difference of just a few hundred bar.

At this point, the question arises as to how much power can be extracted given the limited pressure drop available. Assuming a Darcy flow through the reservoir, one realizes that the mass flow rate is of the form:

$$Q = (4\pi k/v) \ell (P_1 - P_2) \quad (14)$$

k standing for the permeability of the rock and v for the kinematic viscosity of the fluid; ℓ is a characteristic length that will be determined by the number and geometry of the lay out of injection and collection points, and the rock fracture in their neighbourhoods. It will in any case be smaller than the diameter of the reservoir: $\ell < L$.

The mass flow rate will be bound, in step with the bound imposed upon the pressure drive (combining Eqs. (13) and (14)), according to:

$$Q \ll (4\pi k/v) \ell \rho c (T_g - T_\infty)^2 / T_g \quad (15)$$

This upper bound to the flow rate can be estimated at 10 000 kg/s, taking $v \approx 10^{-7}$ m²/s; $\ell \approx 100$ m, and assuming a very low permeability of $k \approx 10^{-14}$ m² [6].

Consequently, following Eqs. (13) and (15), the exergy rate available will be limited to:

$$dE/dt = v Q (P_1 - P_2) \ll (4\pi k/v) \ell \rho c^2 (T_g - T_\infty)^4 / T_g^2 \quad (16)$$

This upper bound is of order of one GW, for the values of parameters assumed so far.

This result is comparable to the average thermal power that can be released in a time scale of one hundred years in a reservoir of about 1km³, as shown in the previous section 2.

In an actual geothermal plant, both pressure drop and flow rate should be kept, and the exergy extraction rate shall attain levels well below the defined bounds.

4 INSTALLED CAPACITY

The foregoing calculations indicate it is quite plausible to have an electric power plant operating on the heat released in a 1 km³ geothermal reservoir fed by the carbonation of mafic or ultramafic rock. In this concept, CO₂ is employed both as chemical reagent and as fluid transfer agent that is being sequestered in the process of heat and power generation. However, it is realized that, in view of thermodynamic constraints, as explained in section 2, and of the upper bounds imposed on the pressure drop and on the flow rate in the geological reservoir, as assessed in section 3, the capacity of such a power plant will in practice be considerably less than the theoretical power straightly derived from the heat released by full carbonation of the reservoir rock.

The estimates of both power and operating life time for such a power plant have to take into account the total amount of thermal energy that can be generated within the geological reservoir, as given by Eq. (6). In our case that amount has been estimated at $H \approx 2.5$ EJ (10^{18} J); however, it will be prudent to assume that the carbonation will proceed up to half way to completion, and that half of the heat effectively released will be spent in heating up the reservoir to the operating temperature level and left there when the heat extraction is halted, so that only about 0.6 EJ might be available to be converted in the power plant. This amount, collected over a lifespan of 50 years, the lifetime of the power plant, would correspond to an average thermal power input of nearly 380 MW.

The thermal (conversion) efficiency of the plant depends on the temperature at which the geothermal heat can be delivered, which has been found to be limited to about 474 to 492 K, depending on the mineralogical composition of the rock. In our case study, the Carnot efficiency will thus be limited to $(T_g - T_\infty)/T_g \approx 0.4$.

We conclude that the available geothermal power can possibly feed an electrical power plant delivering a steady gross power output of up to $W \approx 150$ MW for 50 years. This satisfies the exergy rate bound stated by Eq. (16).

5 CONCLUSIONS

Carbonation of olivines, serpentines, pyroxenes and plagioclases, either in-situ or of mined waste-rock has been proposed as a way of safely disposing of CO₂ and avoid the greenhouse effect from its emission to the atmosphere. The carbonation is an exothermic reaction, so that the heat generated can be employed as a valuable by-product of the CO₂ sequestration.

It is shown that extracting the heat energy generated in a mafic or ultramafic geological reservoir where CO₂ is being sequestered, and converting it to electrical power, is feasible at large

industrial scale, and that the energy and exergy budgets are favourable.

Geological requirements or constraints include favourable fluid trapping structure, sufficient rock permeability, and fracking procedure in setting up the CO₂ injection/collection wells lay out and in maintaining the fluid flow against carbonate and silica precipitation in the fracture network.

Our case study suggests the possibility of generating up to about 65 TWh of electrical energy while capturing permanently about 1Gton CO₂ per 1 km³ of peridotite or basalt rock.

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