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**Title:**

Investigation and comparison of two different paths of serpentinite carbonation.

**Abstract:**

Serpentinite carbonation is a possible tool for reducing CO2 emissions and enhancing the CH4 concentration of biogas (e.g., ZEBU project). The same technique may be also used for asbestos inertization. Two different paths of serpentinite carbonation were investigated through laboratory experiments, adopting a serpentinite sample mainly made up of lizardite, with subordinate orthopyroxene, magnetite, and chromite.

Path 1 consists of dissolution of serpentinite in H2SO4 2M, at 0.1 MPa and 70 °C, followed by addition of NH4OH to the solution, to increase the pH up to 9.5, under a CO2 flux. MgO extraction from the rock turned out to be efficient, varying between 82 to 97%, depending on the reaction time (4 to 24 h). Carbonate minerals did not form due to precipitation of Mg- and NH4- bearing hydrated (or anhydrous) sulphates which caused a considerable Mg depletion of the solution. However, precipitation of nesquehonite, a hydrated Mg carbonate occurred upon mixing, at low temperature, of a synthetic MgCl2 solution (which simulates acid attack carried out using HCl instead of H2SO4) with a solution of (NH4)2CO3, obtained through absorption of CO2 in NH4OH.

Path 2 consists of direct carbonation of serpentinite at high pressure and temperature. In particular, the serpentinite sample was reacted with a NaCl aqueous solution and supercritical CO2 at 9-30 MPa and 250-300 °C, either in a stirred reactor or in externally heated pressure vessel. CO2 was either supplied from a tank (stirrer reactor) or produced from decomposition of oxalic acid or silver oxalate (pressure vessel). Serpentinite carbonation was observed to occur after 24h at 30 MPa, 300 °C in 100 g L-1 NaCl aqueous solutions. Under these conditions, Fe- and Ca- containing magnesite crystallized; the amount of this carbonate mineral varies from 5 to 10 wt%, indicating that the carbonation process is incomplete, as it affects only the outer portion of the rock grains, whose cores seem to remain unreacted.

Further experiments, analyses and computer simulations are under way to investigate the release from serpentinite and fate of trace elements (e.g., Fe, Mn, Ni, Co) as well as their possible incorporation in secondary carbonates produced in both reaction paths.
Zero-Emission methane-poor Biogas Utilization through mineral carbonation:
the ZEBU project

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Abstract

Biogas is mainly composed by CH₄ and CO₂. To be used for electricity generation, biogas must contain at least 40% CH₄ by vol. The composition of biogas is chiefly controlled by decomposition of organic matter under either anaerobic conditions (with production of CH₄ and CO₂) or aerobic conditions (with production of H₂O and CO₂). Both occurrence of the second process or addition of air may decrease CH₄ content making the biogas unsuitable for electricity production.

ZEBU is an innovative two-step process aiming at both: (i) increase CH₄ content of biogas through absorption of CO₂ in an NH₄OH solution (step 1); (ii) sequester CO₂ through mineral carbonation (step 2). The second goal is achieved by mixing, at low T, the (NH₄)₂CO₃ solution obtained in step 1 with a MgCl₂ aqueous solution, leading to precipitation of nesquehonite. After preliminary studies aimed at individuate the best strategy for the overall process, the lab absorption plant was designed and constructed. Its core was a 1-meter-high absorption column filled with Raschig rings and equipped with P- T-, pH-, conductivity- sensors. Also step 2 was tested at the lab scale, confirming that mixing of (NH₄)₂CO₃ with MgCl₂ leads to immediate precipitation of
nesquehonite. The results of laboratory tests were utilized for the final design of the prototype plant. This is made up of two 7-meter-high absorption towers, located on a skid, also hosting tanks, pumps, etc. A second skid was designed and realized for the carbonation reactor and related apparatuses. The ZEBU plant is now installed in a landfill, and tests are under way utilizing a CH₄-poor biogas. We expect that this field experimentation will demonstrate that it is possible: (i) to recover energy from biogas poor in CH₄, which is produced in many landfills and (ii) sequester CO₂ in the stable nesquehonite lattice.

**Keywords:** biogas; landfill; CO₂ absorption; mineral carbonation; nesquehonite.

1. **Introduction**

Gas emission from landfills has a strong impact on atmosphere due to the high greenhouse effects of the two major components of biogas, CO₂ and CH₄. According to Forster et al. (2007), the global warming potential of CH₄ is of particular concern, especially in the short period, as it is 72 times higher than that of CO₂ over a time horizon of 20 years, reducing to 25 over 100 years and 7.6 over 500 years. Today there is a general consensus on the urgent need to drastically reduce inputs of anthropic greenhouse gases into the atmosphere through the adoption of several strategies, as humans do not have a single magic option. The ZEBU project was conceived to provide a contribution, even minimal, to the solution of this common problem, drawing on the technologies of (i) CO₂ absorption in an NH₄OH solution and (ii) mineral carbonation, namely precipitation of nesquehonite [MgCO₃·3H₂O]. In this way, CH₄-poor biogas can be used for electricity generation thus reducing to a significantly extent (if not zeroing) gas emissions into the atmosphere.

In the phase of CO₂ absorption an aqueous (NH₄)₂CO₃ solution is produced. In the subsequent phase of mineral carbonation, this (NH₄)₂CO₃ solution is mixed with an MgCl₂ solution,
which can be obtained through dissolution of serpentine in relatively concentrated HCl. A schematic layout of the whole chemical plant is shown in Figure 1.

![Diagram of the chemical plant](image)

**Figure 1.** Schematic layout of the whole chemical plant comprising: the mill E-1 for serpentine grinding, the reactor E-2 for serpentine dissolution in concentrated HCl, three filtration apparatuses to separate amorphous SiO₂ (E-3), iron oxy-hydroxides (E-5) and Mg carbonates (E-10), the two tanks E-4 and E-6 for pH adjustment through NH₄OH addition, the CO₂ absorption column E-7, the carbonation reactor E-8, and the crystallizer E-9.

Up to present, the following activities were realized in the framework of the ZEBU project to test both chemical processes of interest and the feasibility of the whole approach:

(i) selection of the best strategies and working conditions for CO₂ capture and mineral carbonation of serpentine through laboratory tests;
(ii) dimensioning and designing of the CO\(_2\) capture plant and the carbonation reactor;

(iii) realization of the CO\(_2\) capture plant and the carbonation reactor at the laboratory scale;

(iv) realization of a full-scale prototype plant comprising a CO\(_2\) capture unit and a carbonation unit;

(v) installation of the full-scale prototype plant in the landfill of Montespertoli, near Florence (Italy).

Field tests are still under way in this period. In this communication we intend to present some of the lessons we learned through the activities carried out so far.

2. Biogas chemistry

Disposal of waste containing organic matter in landfills leads to production of biogas, through anaerobic decomposition of organic matter. The process can be schematically represented by the following reaction (Berner and Berner, 1996):

\[
2 \text{CH}_2\text{O} \rightarrow \text{CO}_2(g) + \text{CH}_4(g),
\]

in which organic matter is indicated through the simplified CH\(_2\)O stoichiometry. In spite of this simplification and the complex reactions occurring during the whole organic matter decomposition process, reaction (1) predicts nicely the composition of biogas, which is primarily composed by CO\(_2\) and CH\(_4\) in nearly equal molar (and volume) concentrations.

In the shallow parts of landfills, where penetration of atmospheric O\(_2\) takes place, organic matter decomposes under aerobic conditions. This process can be simplified through the following reaction (Berner and Berner, 1996):

\[
\text{CH}_2\text{O} + \text{O}_2(g) \rightarrow \text{CO}_2(g) + \text{H}_2\text{O}.
\]

Gas originated through reaction (2) is essentially a mixture of CO\(_2\), N\(_2\) and unreacted O\(_2\).

Mixing of this shallow gas with deep-originated biogas leads to gas compositions depleted in CH\(_4\). Occurrence of these undesired processes (aerobic reactions and mixing with biogas) has
huge practical implications, in that this mixed gas or CH₄-poor biogas cannot be used for electricity generation. One of the ZEBU aims is the solution of this problem through absorption of CO₂ and consequent enrichment of biogas in CH₄.

3. Carbon dioxide absorption

A lot of work was carried out in recent years on CO₂ absorption, especially in the framework of Carbon Capture and Sequestration (CCS) projects, whose ultimate aim is the reduction of atmospheric CO₂ concentration (IPCC, 2005). For instance, organic solvents such as monoethanolamine (MEA) and diethanolamine (DEA) were proposed for CO₂ capture based on previous experience in gas purification technology (e.g., Leites, 1998; Aboudheir et al., 2003).

Since presence of CH₄ does not affect CO₂ absorption in organic solvents (Gaur et al., 2010), this approach was adopted at the beginning of the ZEBU project and a plant for CO₂ absorption in MEA, specifically apt for biogas, was designed (Figure 2). Biogas interacts with the organic solvent in the absorption column C₁, where temperature ranges from 40 to 60°C approximately. At these temperatures, CO₂ establishes chemical bounds with the solvent. In the upper part of the absorption column C₁, the CO₂-free biogas is washed with water to remove solvent vapors and entrained droplets. Then it exits from the absorption column C₁ and is sent to the apparatus for the production of electricity. The CO₂-bearing organic solvent is pumped through the reboiler F₁ first and through the stripping column C₂ afterwards, where both solvent regeneration and CO₂ recover occur, at temperatures close to 100-140°C and pressures somewhat higher than the atmospheric value. Pure CO₂ exits from the upper part of the stripping column C₂ and is sent to the carbonation plant. It is necessary to supply heat both at the reboiler F₁, to attain the conditions needed for solvent regeneration, and to produce steam, acting as stripping gas. This heat requirement varies from 3.5 to 11 MJ/kg of CO₂ (Abu-Zahra et al., 2007; Tobiesen et al. 2008)
and represents the major energy-demanding operation of the whole process. Further energy consumptions are due to liquids pumping, biogas transport (realized by the gas fan V1) and compression of produced CO$_2$ (compressor V2). Ancillary equipment needed to maintain the quality of the solvent solution (eliminating its deterioration products, substances generated by corrosion and suspended particulate) is also shown in Figure 2.

![Figure 2. Schematic layout of the CO$_2$ absorption plant using organic solvents.](image)

However, results of laboratory carbonation experiments (see section 4) suggested us to abandon organic solvents and to adopt an alternative route of CO$_2$ absorption, using an aqueous solution of ammonia (4.6% by weight), according to the following reaction:

$$\text{CO}_2(\text{g}) + 2 \text{NH}_4\text{OH}_{(aq)} \rightarrow (\text{NH}_4)_2\text{CO}_3_{(aq)} + \text{H}_2\text{O}. \quad (3)$$

After screening the pertinent scientific literature (e.g., Kurz et al., 1995; Diao et al., 2004; Yeh et al., 2005; Derks and Versteeg, 2009; Liu et al., 2009; Qin et al., 2010; Qin et al., 2011), this process was first tested in the laboratory constructing a small-scale absorption plant comprising a 1-meter-
high column filled with Raschig rings and equipped with pressure-temperature-, pH- and conductivity-sensors. Encouraging results were obtained and a full-scale prototype plant was designed, realized and recently installed in the landfill of Montespertoli, near Florence (Italy).

In this full-scale prototype plant (Figure 3), biogas is taken from the main pipeline and is sent by the gas fan P-1 at the CO₂ absorption unit with a flow rate of 8.4 Nm³/h approximately. Considering the contact surface needed for CO₂ absorption in the aqueous solution of NH₄OH and the consequent height of the absorption unit, this was split in two 7-meter-high absorption towers (C-1 and C-2 in Figure 3).

**Figure 3.** Layout of the full-scale prototype plant, comprising the CO₂ absorption unit, which uses an NH₄OH solution (left part of the figure), and the carbonation unit (right part of the figure).

Biogas enters the lower part of column C-1 where it interacts with a countercurrent flow of partially reacted NH₄OH solution coming from column C-2. Biogas leaving from the upper part of column C-1 is sent in the lower part of column C-2, where it meets the countercurrent flow of unreacted NH₄OH solution entering the upper part of column C-2. Both columns are partly filled
with Raschig rings for over half of their total height, to favor CO₂ absorption in the NH₄OH solution. In addition, the uppermost part of column C-2 hosts a section for washing the gas with water, to absorb ammonia traces possibly present in the CH₄-enriched biogas, which is then sent to the electricity production system. The flow rate of the NH₄OH solution must be kept at 0.4 m³/h approximately both to allow the correct distribution of the liquid phase inside the two columns, in the light of local hydrodynamic conditions, and consequently to favor the CO₂ absorption process.

Changes in the chemistry of the aqueous NH₄OH solution during progressive CO₂ absorption were predicted by means of the software package EQ3/6, version 8.0 (Wolery e Jarek, 2003) and verified analytically during the lab experimental tests carried out using a small-scale absorption plant comprising a 1-meter-high column. Owing to the high ionic strength of the aqueous solutions of interest, it was necessary to compute activity coefficients by means of Pitzer’s equations (e.g., Pitzer, 1987), using the thermodynamic database YPF of EQ3/6, which was previously updated inserting:

(i) the interaction parameters between cationic solutes and CO₂(aq), which are valid from 25 to 150°C (Accornero and Marini, 2009) and include those for the NH₄⁺ - CO₂(aq) couple;

(ii) the interaction parameters between cationic solutes and SiO₂(aq), whose range of applicability extends from 25 to 300°C (Accornero and Marini, 2009);

(iii) the interaction parameters for the couples NH₄⁺ - HCO₃⁻, NH₄⁺ - CO₃²⁻, NH₃ - HCO₃⁻ and NH₃ - CO₃²⁻, given by Kurz et al. (1995), which can be used from 40 to 200°C;

(iv) the solubility product of NH₄HCO₃, which was estimated based on the data reported in the CRC manual (Lide, 2001) for the temperature range 0-100°C.
Carbamate ion (NH$_2$COO$^-$) was not taken into account in the EQ6 simulations, which were carried out at fixed temperature and pressure of 25°C and 1.013 bar, respectively, working in stoichiometric mode, that is with respect to the reaction progress variable, neglecting the kinetics of relevant processes. Analytical data are in good agreement with computed data (Figure 4), suggesting that the CO$_2$ absorption process, which occurs at constant total alkalinity, is conveniently monitored by pH measurement.

4. Laboratory experiments to select the best strategy and working conditions for the mineral carbonation of serpentine

Based on a preliminary review of the pertinent literature, it is evident that two distinct reaction paths of mineral carbonation of serpentine were investigated so far, either (i) acid dissolution, followed by pH adjustment and CO$_2$ addition at low temperatures and pressures or (ii) direct serpentine-CO$_2$-H$_2$O ($\pm$ NaCl) interaction at high temperatures, pressures and P$_{CO_2}$ values.
A very interesting investigation of the low T-P processes was carried out by Teir and coworkers (Teir et al., 2007a; Teir et al., 2007b) who highlighted that serpentinite can be converted to a large extent (80–90%) into pure hydromagnesite \[ \text{Mg}_5(\text{CO}_3)_4(\text{OH})_2 \cdot 4\text{H}_2\text{O} \] through acid dissolution at 70 °C and 1 bar, followed by NaOH addition (to adjust pH close to 9) and CO\(_2\) interaction.

Among the results of high T-P processes, it is worth to recall that:

(i) At 155 °C, under a \(P_{\text{CO}_2}\) of 185 bar, carbonation occurs efficiently (close to 78%) in 30 minutes, starting from pre-heated serpentine (2h at 630 °C) and reacting it with aqueous solutions containing 15% NaCl-NaHCO\(_3\) (O’Connor et al., 2001).

(ii) At 280 °C and a \(P_{\text{CO}_2}\) of 235 bar, a much lower carbonation of pre-heated serpenties was observed in aqueous solutions of similar chemistry (Jia et al., 2004).

(iii) Two 4h-long experiments at 400 and 500 °C and a much higher total pressure (1 kbar), carried out using untreated chrysotile and pure water lead to a CO\(_2\) sequestration of 11-12 mol% only (Dufaud et al., 2009).

Starting from this scenario, we decided to investigate experimentally the mineral carbonation of a selected serpentinite, mainly constituted by lizardite \[ \text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4 \], with subordinate orthopyroxene \[ (\text{Mg, Fe})_2\text{Si}_2\text{O}_6 \], magnetite \[ \text{Fe}_3\text{O}_4 \], and chromite \[ \text{FeCr}_2\text{O}_4 \], through both (i) pre-dissolution in 2M H\(_2\)SO\(_4\) at 1 bar, 70 °C and (ii) direct rock-CO\(_2\)-H\(_2\)O (± NaCl) interaction at higher temperatures and pressures, up to 300 °C and 300 bar (see Orlando et al., 2011 for further details). The selected serpentinite was grinded and sieved to separate different granulometric fractions, which were characterised through N\(_2\) sorption and desorption at 77 K, to measure the Brunauer-Emmett-Teller (BET) specific surface area and related parameters.

In the low T-P experiments, the serpentinite was reacted with an acid solution (H\(_2\)SO\(_4\) 2M) over different times (up to 24h). MgO extraction from the rock turned out to be efficient, varying
between 82 to 97%, depending upon the reaction time. Calculated dissolution rates vary from $4.0 \times 10^{-9}$ to $8.5 \times 10^{-10}$ mole m$^{-2}$ s$^{-1}$. Carbonation tests were subsequently performed rising the pH of the solutions up to 8.5 to 9.5 (through addition of NH$_3$ solution) under a CO$_2$ flux, but they failed since Mg- and NH$_4$- bearing hydrated (or anhydrous) sulphates precipitated causing a considerable Mg depletion of the solutions. In contrast, precipitation of a Mg-hydrated carbonate, nesquehonite, occurred upon mixing a synthetic MgCl$_2$ solution (which simulates acid attack performed using HCl instead of H$_2$SO$_4$) with a solution of (NH$_4$)$_2$CO$_3$, obtained through absorption of CO$_2$ in ammonia (see section 5).

In the high T-P experiments, the serpentinite was reacted with a NaCl-bearing aqueous solution and supercritical CO$_2$ at 90-300 bar and 250-300 °C, either in a stirred stainless-steel reactor Parr series 5500 or in externally-heated pressure vessel apparatus (Leco Corp., model HR-2B-2), loading the starting material into Au capsules which were welded shut and introduced into the vessel. Carbon dioxide was either supplied to the stirrer reactor from a CO$_2$ tank or produced in the pressure vessel through decomposition of oxalic acid or silver oxalate. Serpentinite carbonation occurs after 24h at 300 bar, 300°C in 100 g L$^{-1}$ NaCl aqueous solutions leading to crystallization of Fe-, Ca-containing magnesite [MgCO$_3$], whose amount varies from 5 to 10 wt%. Assuming the serpentinite to be constituted by pure lizardite only, the calculated dissolution rates under these conditions range from $6.3 \times 10^{-11}$ to $1.3 \times 10^{-10}$ mole m$^{-2}$ s$^{-1}$.

Although single-step carbonation proceeds to a significant extent in a relatively short time under high P-T conditions, transformation of serpentinite in carbonates and by-products is incomplete, as it affects the outer parts of rock grains only, whose cores remain unreacted. Therefore we decided to adopt the low T-P carbonation route, consisting of dissolution in concentrated HCl, followed by pH adjustment and mixing with a solution of (NH$_4$)$_2$CO$_3$, obtained through absorption of CO$_2$ in ammonia.
5. Low T-P mineral carbonation

Owing to the complexities and difficulties of the whole chemical process, the limited time schedule for the completion of the ZEBU project, and economic constraints, we decided to realize only a part of the full-scale prototype plant, namely the CO₂ absorption unit (already described in section 3) and the carbonation unit, representing the major challenges of the ZEBU project, whereas the following parts were not constructed (Figure 1):

(i) Unit for grinding the serpentinite, as it requires high-quality, high-costs apparatuses to avoid the environmental dispersion of fine fibrous particles.

(ii) Unit for serpentinite dissolution, as the main problems to be solved are related to solid/solution separations. In fact secondary solids are formed both during incongruent dissolution of serpentinite minerals (chiefly amorphous silica) and during the neutralization of the aqueous solution up to pH values of 8.5 to 9.5 (chiefly oxy-hydroxides of trivalent Fe).

Based on the results of laboratory experiments outlined in section 4, a laboratory-scale carbonation reactor was constructed and used to test the carbonation reaction:

\[ \text{MgCl}_2(\text{aq}) + (\text{NH}_4)_2\text{CO}_3(\text{aq}) \rightarrow \text{MgCO}_3(\text{s}) + 2\text{NH}_4\text{Cl}(\text{aq}). \]  

(4)

occurring through mixing of the (NH₄)₂CO₃ aqueous solution (which is produced by CO₂ absorption in ammonia), with a synthetic MgCl₂ aqueous solution (which simulates the product of serpentinite dissolution in concentrated HCl followed by pH adjustment and filtration of by-products).

Expected chemical variations in the (NH₄)₂CO₃ aqueous solution upon progressive addition of MgCl₂ 1M were computed using the software package EQ3/6, version 8.0 (Wolery e Jarek, 2003) and the thermodynamic database YPF, previously improved as described in section 3. Again, owing to the high ionic strength of the two aqueous solutions, activity coefficients were calculated by means of Pitzer’s equations. Temperature and pressure were fixed at 25°C and 1.013 bar,
respectively. The simulation was performed with respect to the reaction progress variable, leaving kinetics out of consideration. As shown in Figure 5, there is a good agreement between analytical and computed alkalinity, which is a suitable parameter to monitor the advancement of the carbonation/precipitation reaction.

**Figure 5.** Alkalinity changes during progressive addition of the MgCl₂ 1 M solution to the (NH₄)₂CO₃ aqueous solution produced by CO₂ absorption in ammonia.

Precipitating Mg carbonates were characterized through XRD, whose results (Figure 6) confirm the presence of prevailing nesquehonite with minor amounts of magnesite.
Figure 6. XRD spectra of four Mg-carbonate samples (lines of different colors) precipitated through mixing of (NH$_4$)$_2$CO$_3$ with MgCl$_2$. The main peaks of magnesite and nesquehonite are indicated for comparison.

The occurrence of nesquehonite precipitation is in agreement with the results of previous studies (e.g., Wang et al., 2008; Dong et al., 2009; Ferrini et al., 2009; Saldi et al., 2009). Below 80-120°C, metastable hydrous Mg-carbonates form instead of magnesite due to kinetic factors, chiefly the high activation energy and the slow step advancement rates of the spiral growth mechanism controlling magnesite precipitation (Saldi et al., 2009). According Wang et al. (2008), homogeneous (unseeded) precipitation of nesquehonite by the reaction of MgCl$_2$ with (NH$_4$)$_2$CO$_3$ in supersaturated solutions is affected by several parameters, including reaction temperature, initial concentration, titration speed, stirring speed, and equilibration time, with the first three having significant effects on crystal morphology and particle size of nesquehonite. Under optimized operating conditions, nesquehonite crystals attain length and width of ~40 and ~5 mm, respectively, acquiring good filtration properties.

Based on the experimental results obtained from the laboratory-scale carbonation reactor, the carbonation unit of the full-scale prototype plant was designed and constructed (Figure 3, right part). It comprises: the stirred reactor R-1, which can be heated up to a maximum temperature of
80°C, the crystallizer S-1, the filtration apparatus F-1 and the tanks D-7 and D-8 for the collection of the separated NH₄Cl solution and solid Mg-carbonates.

6. Conclusions

All the activities carried out so far in the ZEBU project, comprising both preliminary studies aimed at individuate the best strategy for the overall process and experimental tests performed by means of a laboratory-scale plant, were finalized to design and construct a full-scale prototype plant. Similar to the laboratory-scale plant, the full-scale prototype plant is made up of:

(i) a CO₂ absorption unit, including two 7-meter-high absorption towers, located on a skid, also hosting tanks, pumps etc., and
(ii) a carbonation unit, installed on a second skid and comprising the carbonation reactor and other apparatuses.

The full-scale prototype plant is now installed in the landfill of Montespertoli, near Florence (Italy), where experimental work is under way. We are confident that on-going field tests will prove the feasibility of:

(i) energy recovery from CH₄-poor biogas, which is produced in many landfills and
(ii) CO₂ incorporation in the stable lattice of Mg-carbonates, such as nesquehonite and magnesite.

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7. References


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