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GAS GEOCHEMISTRY OF THE DOGGER GEOTHERMAL AQUIFER
(PARIS BASIN, FRANCE)

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ABSTRACT

The low enthalpy program developed in the Paris Basin provides the opportunity for studying the gas geochemistry of the calcareous aquifer of the Dogger. Hydrocarbons and CO₂ are mainly biogenic, He displays high concentrations. He, Ar and N₂ have multiple origins (radioactive decay, atmospheric migration, biochemical processes). The distribution of the gases in the zones of the basin varies in relation to the general chemistry, sedimentology and hydrodynamics. The gas geothermometers do not apply to this environment but useful estimations of the redox potential of the fluid can be derived from CO₂/CH₄ and N₂/NH₃ ratios. H₂ and H₂S are involved in corrosion processes and scaling in the pipes.

INTRODUCTION

Gas geochemistry has been used extensively for reservoir engineering purposes in high enthalpy geothermal environments (amongst others, Arnorsson and Gunnlaugsson, 1985; D’Amore and Panichi, 1980; Giggenbach, 1980), but has been less often used in low enthalpy geothermal reservoirs.

The Dogger sedimentary aquifer mainly consists of carbonate facies. It has been exploited for geothermal purposes since 1970. The salinity of the fluids varies from 6.5 to 35 g/l and the downhole temperatures at depths ranging from 1600 to 1850 m are between 47 and 85 °C (Rojas et al., this volume).

The chemistry of this reservoir was shown to be very complex by Bastide (1985) and Criaud et al. (1986). The heterogeneities observed in chemical and isotope compositions are presently best explained by the evolution of paleoseawater which has undergone partial evaporation, diagenesis and mixing phenomena involving several components having variable temperature and mineralization. The combination of different studies (isotopes, conservative elements, water-rock interaction processes) allows the distinction of several areas with various fluid evolutions, bacterial reduction (Fouillac et al., 1986) mixing processes, rock interactions (Rojas et al., this volume).

We present some preliminary results concerning the gas chemistry of the reservoir. The gas analyses all display typical compositions of the natural gas generally found in sedimentary rocks, with hydrocarbons, including methane, of which the concentration is as much as 50% of the gas content, the remainder, includes nitrogen, CO₂ and rare gases.

The aim of this study is: (1) To provide a complete set of gas data at a regional scale; (2) To use this tool for a better comprehension of the origin and circulation of fluids in the Paris Basin.

Among the various gases we will distinguish the inert species (rare gases, N₂) and the components undergoing chemical reactions (CO₂, H₂). CO₂, CH₄, to a certain extent H₂S, H₂ and N₂ can be used for redox considerations and thermodynamics.

SAMPLING AND ANALYTICAL PROCEDURES

All the gases were sampled at the wellheads either at the end of the drilling tests (artesian flow) or later during production (all wells equipped with pumps). A line of the fluid under pressure is taken from the main pipe and diverted to a Pyrex glass degassing system operating at atmospheric pressure. After purging, “free gas” was collected in a glass container with two vacuum stopcocks. A flask under vacuum closed by a teflon stopcock was half filled with the separated liquid phase, thus containing the dissolved gases and microbubbles of free gas.

During these operations the flow rate was kept constant and the gas/liquid ratio (GLR) was measured with a reproducibility of 6-7%. Important variations were sometimes observed when sampling at different times. These variations are attributed to changes in working conditions, sampling pressure, temperature or the presence of water vapor giving rise to an overestimated gas/liquid ratio, or a combination of these processes. The GLR were used to recalculate the total...
gas content (free + dissolved) of the fluid.

The gas analyses were performed by gas chromatography except for a few recent He results determined in the field by mass spectrometry (Marty et al., in prep.). The gas analyses for free and dissolved gases are given in tables 1 and 2.

A notable oxygen content of 0.1 to 5% is present in some of the samples, and is hardly compatible with the reduced character of the water which contains dissolved hydrogen sulphide and displays low redox potentials. Only a few ppb of dissolved O$_2$ was detected onsite by the colorimetric method. The real concentration may be much lower. We conclude that the oxygen originated outside the Dogger aquifer and could result from air contamination during sampling or analytical procedures. Consequently, before interpretation, the "true" O$_2$ content was assumed to be zero, N$_2$ and Ar were corrected correspondingly, the effect being negligible for other gases.

**GENERAL PATTERNS OF GAS DISTRIBUTION**

In order to classify the zones of the aquifer, the results were reported on figure 1 according to the major components (N$_2$, CO$_2$, hydrocarbons). Despite a wide range it is clear that the southernmost samples are enriched in methane and other light hydrocarbons, while the proportion of nitrogen increases in the Seine-St-Denis areas and in samples from the border of the basin.

CO$_2$ is directly involved in equilibrium with minerals such as calcite and dolomite but the calculated partial pressure varies within the basin (Bastide, 1985). No relation was found between the total CO$_2$ content and the temperature or salinity. However, the concentration of methane is related to the temperature (Fig. 2) within the basin.

**INERT GASES**

The samples present very high helium concentrations (0.5-1.5%) when compared to the air content (5.24 ppm) and magmatic gases (a few ppm). Similar high He contents are found in some sedimentary basin gas reservoirs (e.g. the Texas Panhandle, Sartman et al., 1961) and result from the accumulation of $^4$He produced from the decay of U+Th over a long period. Several attempts to date underground fluids have been successful, providing that reservoir parameters such as porosity, U+Th contents of wall rocks are known (e.g. Marine, 1979). In the case of the Dogger, these parameters are presently poorly constrained and any quantitative dating attempt would be unrealistic. The high He concentrations nevertheless indicate that the fluids are old, and part of them may be contemporaneous with the sedimentary wall rocks. Alternatively, part of the helium may result from the migration of He from deeper strata, and accumulation in the Dogger aquifer. Dating methods, including the use of Rn will be discussed elsewhere.

When plotted on a N$_2$-Ar-He diagram (not given here) all samples can be interpreted as resulting from mixing between the following components:

1. An atmospheric component as defined by negligible He contents, and a N$_2$/Ar ratio between 83.6 and 40 (but the latter corresponds to either air mixing or limited outgassing of the fluid; the lower limit of N$_2$/Ar=40 corresponds to the solubility ratio of air gases, when outgassing occurs at a steady rate).
2. A radiogenic component defined as having a He/Ar ratio of between 2 and 4, and corresponding to a chondritic composition for the parents U+Th and K.

Other information can be gained when considering absolute abundances. The calculated total N$_2$ content exceeds by about a factor of 10 the ASW concentration, which shows that part of the nitrogen present results from biogenic processes. This is also reflected in the N$_2$/Ar ratio which exceeds the air value in some cases. Unfortunately non-radiogenic rare gas data are not available and the biogenic N$_2$ addition cannot be quantified. The He/N$_2$ ratio is fairly constant, around 0.02, and indicates that $^4$He production and N$_2$ addition occurred at similar rates for the different study areas.

The contour tracing He contents over the Paris Basin area (Fig. 3) are consistent with the general flow pattern derived from hydrodynamic studies and reveals a south-southeast trending gradient also indicated by other chemical parameters. The more evolved waters (high sulphide content) of Seine-St-Denis and north of the basin show an increase in the He content. In accord with this hypothesis, some recharge is thought to occur at the southeast border of the basin (Morvan area). Surprisingly, the He content is negatively correlated with the downhole temperature. A single heat flux model radiogenic input correlation, as is generally inferred, is clearly not applicable in this case. A detailed study of the production and mixing strata could clear up this inversion problem.

The picture derived from inert gases is consistent with the chemistry of the reservoir, which indicates mixing involving paleoseawater, recent fluids and diagenetic processes.
**GAS GEOTHERMOMETRY**

In geothermal environments the composition of the gas phase is frequently controlled by a chemical equilibrium so temperatures can be derived from gas analysis. When applying the formula of D’Amore and Panichi (1980) a great uncertainty is introduced if the hydrogen or hydrogen sulphide percentage (not always satisfactorily determined for this study) is overestimated. Nevertheless, comparisons between calculated and measured temperatures always lead to much higher estimated temperatures (100-150 °C) than downhole measurements. Evidently the Fischer-Tropsch reaction cannot explain the concentrations of methane found in this sedimentary environment, and H₂S, H₂ and CO₂, partly biogenic, are not fixed through equilibrium with mineral buffers. Corrosion may produce noticeable amounts of H₂, as proved by the variations at different sampling times, and H₂S is involved in iron sulphide scaling.

Likewise, the gas geothermometers of Arnorsson and Gunnlaugsson (1985) do not apply to this type of geothermal environment and because of the organic processes responsible for the occurrence of CO₂ there is no relationship between total CO₂ and temperature.

**REDOX CONDITIONS IN THE RESERVOIR**

Oxidation-reduction reactions are biochemically mediated in the waters studied, so that we may assume a partial redox equilibrium even at these moderate temperatures. We have shown (IMRG annual report, 1985) that the platinum electrode only provides, in this particular case, a measurement of pH₂S and is not related to the "true" redox potential. CH₄/CO₂, N₂/NH₄⁺, H₂ or H₂S/SO₄²⁻ can thus be used to estimate a redox potential according to the reactions:

1. \( \text{CO}_2^+ + 8\text{H}^+ + 8\text{e}^- = \text{CH}_4^+ + 2\text{H}_2\text{O} \)
2. \( \text{N}_2^+ + 8\text{H}^+ + 8\text{e}^- = 2\text{NH}_4^+ \)
3. \( 2\text{H}^+ + 2\text{e}^- = \text{H}_2 \)
4. \( \text{H}_2\text{SO}_4^- + 4\text{H}_2\text{O} = \text{SO}_4^{2-} + 10\text{H}^+ + 8\text{e}^- \)

The pH of the reservoir was computed from surface pH and chemistry, then (H₂S)⁺ and (CO₂)⁺ were calculated. The sulphate and NH₄⁺ concentrations at wellheads were respectively between 600 to 1200, and 18 to 36 mg/l and assumed to be the same in the reservoir. The total sulphide content varies from less than 0.1 mg/l to 100 mg/l. Activities were used instead of concentrations because of the mineralization.

The results of the calculations are summarized below (expressed in mV/NHE). Despite an uncertainty estimated to be at least 15%, an increase of the potentials with temperature is generally observed for the CO₂/CH₄, N₂/NH₄⁺ and H₂ pairs.

<table>
<thead>
<tr>
<th>Potential</th>
<th>Minimum</th>
<th>Maximum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt electrode</td>
<td>-175</td>
<td>+67</td>
</tr>
<tr>
<td>H₂S⁺/SO₄⁻</td>
<td>-250</td>
<td>-190</td>
</tr>
<tr>
<td>CO₂/CH₄</td>
<td>-315</td>
<td>-250</td>
</tr>
<tr>
<td>N₂/NH₄⁺</td>
<td>-320</td>
<td>-240</td>
</tr>
<tr>
<td>H₂/H⁺</td>
<td>-420</td>
<td>-350</td>
</tr>
</tbody>
</table>

The differences could be explained by a non-global redox equilibrium in the reservoir. As explained earlier, H₂ and H₂S are suspected to participate in the corrosion and scaling mechanisms (Pouilliac et al., 1986). Moreover it is not known whether HS⁻/SO₄²⁻ could have achieved equilibrium at these relatively low temperatures, so the CO₂/CH₄ value is probably the more reliable and in accordance with the N₂/NH₄⁺ calculated potentials.

This method provides an accurate value of the redox potential, which is fairly constant at a regional scale, and has been used successfully for calculations to predict the deposition of corrosion products. The observed mineral phases correspond to the minerals found theoretically close to equilibrium with the fluids. The corrosion properties and scaling tendencies of the water from the Dogger aquifer are important parameters for reservoir engineering considerations.

**CONCLUSIONS**

The gas contents display large variations at a regional scale that reflect the evolution of the fluids during diagenesis, aging and mixing phenomena. The geographic trends are comparable to that observed from the chemistry of the water to the northwest.

The high helium contents show evidence for an old component attributed to paleo-seawater. The helium concentration contours are consistent with the general hydrodynamics in the basin, with a recent recharge in the south-southeast margin of the basin.

The gas geothermometers used in geothermics do not apply to this sedimentary environment, most of the reactive gases resulting from biochemical processes.

The redox potential of the reservoir was estimated using CO₂ and CH₄ concentrations. This value, instead of a direct measurement of the potential, was proved to be useful for the characterization of the corrosion and scaling potential which play a major role in reservoir engineering of the Dogger aquifer. At the present time further investigations are needed to find out if the H₂ could be used as an aid in the early detection of corrosion processes.
ACKNOWLEDGEMENTS

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REFERENCES


Institut Mixte de Recherches Géothermiques, "Rapport annuel 1985 (BRGM/APME),".


Figure 1: Diagram CO₂ - N₂ - hydrocarbons
### Table 1: Analysis of free gases in volume %

<table>
<thead>
<tr>
<th>Component</th>
<th>Value</th>
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<tbody>
<tr>
<td>H&lt;sub&gt;2&lt;/sub&gt;</td>
<td>12.0</td>
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<tr>
<td>C&lt;sub&gt;2&lt;/sub&gt;H&lt;sub&gt;6&lt;/sub&gt;</td>
<td>3.2</td>
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<td>CH&lt;sub&gt;4&lt;/sub&gt;</td>
<td>1.6</td>
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</tr>
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<td>C&lt;sub&gt;4&lt;/sub&gt;H&lt;sub&gt;10&lt;/sub&gt;</td>
<td>2.4</td>
</tr>
<tr>
<td>C&lt;sub&gt;5&lt;/sub&gt;H&lt;sub&gt;12&lt;/sub&gt;</td>
<td>2.2</td>
</tr>
<tr>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;14&lt;/sub&gt;</td>
<td>1.5</td>
</tr>
<tr>
<td>H&lt;sub&gt;2&lt;/sub&gt;S</td>
<td>0.7</td>
</tr>
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</table>

- **Temp (°C)**: 35
- **MI**: 19
- **Table 1**: Analysis of free gases

Note: The table provides a detailed analysis of various gases present in a sample, with volume percentages as indicated.
Figure 2: Correlation between CH₄ content and downhole temperature.

Figure 3: Helium concentrations measured at the head of the geothermal wells. Relative percentages instead of absolute concentrations were used because of the uncertainties on GLR and missing data.

<table>
<thead>
<tr>
<th>Date</th>
<th>GAY1</th>
<th>GAY2</th>
<th>GAY3</th>
<th>GB92</th>
<th>GB93</th>
<th>GCRB</th>
<th>GCPR2</th>
<th>GCPR1</th>
<th>GCL1</th>
<th>GCRB4</th>
<th>GCRB5</th>
<th>GCRB6</th>
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</tr>
<tr>
<td>Temp (°C)</td>
<td>71.6</td>
<td>70.7</td>
<td>47.3</td>
<td>65.8</td>
<td>78.2</td>
<td>70.8</td>
<td>70.8</td>
<td>58</td>
<td>58.6</td>
<td>56.4</td>
<td>19</td>
<td>23</td>
<td>48</td>
<td>19</td>
</tr>
</tbody>
</table>

Table 2: Total gas (dissolved + free) contents of the fluids expressed in moles/l