# EVALUATION OF THE TOXICITY OF A MIXTURE OF GEOTHERMAL AND FRESH GROUNDWATER IN CASE OF PERFORATION OF WELL CASING

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## Abstract

Carbon steel casings of geothermal wells exploiting the Dogger aquifer in the Paris Basin are subject to corrosion due to the agressivity of the geothermal fluid containing $Cl^-$, $HS^-/H_2S$, and $HCO_3^-/CO_2$ When localized, this corrosion can lead to perforation of the *casing*. thereby increasing the risk of contamination by geothermal fluids of the freshwater aquifers through which these geothermal casings pass. These aquifers are used as a drinking water resource in the Paris region. The evaluation of the toxicity of the Dagger fluid is based on the toxicity of the chemical species, the sulphate reducing bacteria (SRB) and the surfactant used for anticorrosion treatment. The maximum percentage of Dogger fluid acceptable in freshwater aquifers was calculated for each chemical species concerned (the chemical composition of mixtures of these two types of water were compared to European community drinking water standards). Species were classified by decreasing toxicity taking into account their concentration in the geothermal fluid. The less tolerable species are $Na^+$, $NH_4^+$, $Cl^-$, $H_2S$, phenols and dissolved hydrocarbons. The more toxic species are Be, Cd, Sb, Se, and V. Surfactants in the concentrations used do not represent a danger to human health and are degradable. This is also true for SRB but these bacteria can be active in the drinking water pipes with, as a consequence, corrosion of these pipes and an increase in iron and sulphide contents.

## 1. INTRODUCTION

The waters of the Dogger aquifer (Middle Jurassic) supplying geothermal power plants have a total dissolved salts ranging between 6 to 35 g/l and a temperature ranging from 45 to 85 °C, making them not only unfit for human consumption, but also for discharge at the surface, hence their exploitation by the doublet technique We shall deal below with the risks of pollution of the freshwater aquifers of the Paris Basin by that of the Dogger. These risks are incurred by perforation of a steel well casing and poor casing cementation. The direction of transfer of the water depends on *the* pressure on either aide of the perforated casing This perforation is the result of local casing corrosion due to chemical agressivity of the water.

## 2. DEFINITION OF A DRINKING WATER

The Circular of 15 March 1962 of the French Ministry of Health (Dupont, 1986) defines the properties of drinking waters and the conditions that they must satisfy. These properties were taken up and slightly modified by the European Community in its Official Journal of 30 August 1980 (OJEC). These properties can be divided into five categories

- Organoleptic parameters: a drinking water must be fresh and clear, free of colour, as well as odour and unpleasant taste.
- Physico-chemical parameters: temperature, pH, conductivity, as well as the concentrations of the main chemical species (sodium, potassium, magnesium, calcium. chlorine, sulphates).
- Maximum contents of undesirable species (iron, cobalt, copper. zinc, nitrates. organic carbon, dissolved hydrocarbons. phenols, surface-active agents, suspended matter).
- Maximum contents of toxic species (cyanides, beryllium, arsenic, selenium, heavy metals, pesticides and polycyclic aromatic hydrocarbons (PAH).
- Microbiological paramerers: drinking water must not contain pathogenic or parasitic organisms, or algae.

## 2. CHARACTERISTICS OF THE PARIS BASIN AQUIFERS

### 2.1 Characteristics of freshwater aquifers

These aquifers are located above that of the Dogger of the Paris Basin. They are usually grouped by geological age. Three groups can be distinguished starting from the first deposited

- Lower Cretaceous Albian and Neocomian sands:
- Upper Cretaceous: chalk,
- Lower Tertiary: Fontainebleau Sands. Brie and Saint Ouen limestone.

These aquifers (especially the chalk and Albian aquifers) represent the principal drinking water resource of the Paris area With rare exceptions, the chemical analysis of the species dissolved in these waters reveals that they meet the drinkability standards set by the European Community

### 2.2 Characteristics of the Dogger aquifer

The first geothermal well tapping the Dogger waters was drilled in 1969 to supply the Melun-L'Almont geothermal power plant Since then, and especially in the 1980s. about 110 geothermal wells have been drilled (corresponding to 55 geothermal plants). Geothermal energy emerged at the time as a new, clean and renewable energy source in a period marked by steadily rising energy needs and the difficult recovery from the two oil shocks of the 1970s.

The salinity of the Dogger geothermal water is comparable to that of sea water. It consists essentially of sodium chloride. although there are other major species such as alkali and alkaline earth metals ($K^+$, $Mg^{2+}$, $Ca^{2+}$), sulphates and bicarbonates In addition, Dogger water contains dissolved gases, both neutral ($N_2$, $CH_4$) and acid ($H_2S$, $CO_2$) The later, especially $H_2S$, tend to attack metal well casings, causing corrosion and scaling which, depending on the circumstances. may lead to perforation and/or clogging of the casing (Honegger *et al.*, 1986, 1989; Ignatiadis *et al.*, 1994; Abou Akar and Lafforgue, 1993). The distribution of dissolved $H_2S$ is not uniform: the wells in the north of the Paris Basin have a higher $H_2S$ content than the wells in the south (Ignatiadis, 1994). The relatively high salinity of this water, together with the presence of corrosive gases ($CO_2$, $H_2S$) and traces of certain detrimental species has required their exploitation by using the doublet system the use of a second well for reinjection of this geothermal water. It should also be mentioned that there are differences in the water provided by the different aquifers in the Paris region (Rojas *et al.*, 1989). Temperature varies from 45°C to 85°C, salinity from approximately *6* 5 to *35 g/l* The pH of the fluids in the Dogger carbonate reservoir is low when the dissolved mineral content is high, but shows no relationship with temperature It is primarily determined by the concentrations of carbonated species ($H_2CO_3/HCO_3^-$).

The most significant (and the most influential) chemical characteristic of the Dogger water is its sulphide content. This varies from a few mg/l in the south of the Paris Basin to 80 or even more mg/l in certain wells in the north. The sulphide content of the water from the Dogger aquifer of the Paris Basin has been mapped by Ignatiadis *et al.*, (1991); Ignatiadis (1994), who showed that sulphide content increases along a south-east/north-west axis. It should also he noted that the concentration of sulphides in water which initially had a low sulphide content (wells in the south and east) has increased since operations startcd. This increase is due to the activity of sulphate-reducing bacteria whish convert sulphates into sulphides and thus encourage casing corrosion and scale formation.

Even if the risk of corrosion of carbon steel (API K55) was underestimated, a number of precautions were taken in order to limit damage in the event of casing perforation: double casing is often used at depths (Longin *et al.*, 1994) corresponding to those of deep ground water (Neocomian, Albian) or shallow ground water; cementation of intrr-casing. (inside the double casing) and casing/rock space.

## 3. TOXICITY OF DOGGER WATERS

The geothermat waters are untit for human consumption because of

- chemical composition: high levels of salinity. presence of toxic and undesirable species (heavy metals, dissolved hydrocarbons),
- microflora content,
- the consequences of injecting multi-purpose chemical additives downhole in the production well: bactericide, corrosion inhibition and anti-scale.

### 3.1 Chemical species present in the Dogger watcrs making them unfit for cnnsumption

The chemistry of the Dogger watcrs makes them unfit for human consumption. Besides their mineralization, it is interesting to make a close examination of their contents of toxic and undesirable species, io compare them with the maximum content tolerated in drinking water as set by the European Community, and finally to express, for each of these species, its LD 50 (lethal dose necessary to kill 50% of a given population related to units of weight) expressed in mg/kg of rat unless otherwise specified.

Toxic species

The toxic species in drinking water are:

- metals: arsenic, beryllium, cadmium, chromium, mercury, nickel, lead. antimony, selenium and vanadium;
- organic matter: pesticides, cyanides, PAH;
- pathogenic organisms: foccal coliforms, foccal streptococci, foccal bacteriophages, salmonelli, pathogenic staphylococci, sulphate-reducing clostridiums, enterovirus, etc .

Table 1 shows the maximum permissible content in drinking water for rhese metals and organic matter, their minimum and maximum contents in the Dogger waters nf the Pans Basin, and their LD 50, Since these simple species are ofien insoluble in water (Dogger water samples are prefiltered), we have listed the LD 50 of their soluble salts (Merck catalogue, 1992/93), and recalculated LD 50 for the simple specks Some data relating tu humans have been added to this table. (Casarett and Doull's, 1991 and 'Encyclopedic Médico-chirurgicale"). The minimum lethal dosc (LD min) corresponds to the minimum amount necessary to kill a living being (again expressed per unir of weight). The examination of the LD 50 figures shows that it is difficult to extrapolate from the rat (or the animal considered) to humans. In actual fact, aiid depending on the species concerned, humans can tolerate more (as for mercury and cadmium) , have a similar tolerance (as for arsenic), or tolcrate much less (as with Paraquat considered to be the most tonic herbicide fur man).

The contents of 2200 and 2100 mg/l for arsenic and vanadium respectively should be considered as exceptional, and could be attributed to the recent cleaning of the wells in which they were observed. The maximum contents usually determined are in the range of 200 mg/l, and a recent sampling of two wells representative of the areas nonh and south of the Paris Basin revealcd even lower contents (figures in parentheses). These high contents nevertheless indicate the risk of greater pollution in the case of perforation during a cleaning operation

Undesirable species

The undesirable species are.

- metals: iron, manganese, copper, zinc, cobalt. barium, silver;
- inorganic matter: nitrates, nitrites, ammonium, nitrogen, hydrogen sulphide, boron, phosphorous, fluorine ond residual chlorine:
- organic matter total organic carbun, dissolved or emulsified hydrocarbons, mineral oils: phenols. surfactants, other organo-chlorinated compounds;
- species extractible with chloroform. suspended matter.

Table 1. Toxic species maximum permissible concentrations (M P.C) In drinking water, concentralions in Dogger water and lethal doses. values between parentheses correspond to recent sampling carried out on two wells (north and south of Paris), the others correspond to older analyses.

(*) after cleaning the well

(**) total contents of species defined in rhe OJEC.

(!): from Merck catalogue (▮). from Casarett and Doulls, 1931

(+) trom 'Encyclopédic Médico-chirurgicale"

| chemical species | M.P.C. (µg/l) (OJCE) | concentration in Dogger Waters (µg/l) | LD 50 (mg/kg of rat) | LD 50 (mg/kg of rat) |
|---|---|---|---|---|
| mercury | 1 | < 10 (< 3) | 1 ($HgCl_2$), (LD min = 29 for humans)(!) | 0 74 (Hg) |
| cadmium | 5 | < 55 (< 25) | 310 ($CdCO_3$)(!) (for mouse). (LD of Cd=250 to-1500 for humans)(+) | 202 (Cd) |
| antimony | 10 | 462 (< 50) | 525 ($SbCl_3$)(!) | 280 (Sb) |
| selenium | 10 | (< 25) | unknown for $SeCl_4$ | 6700 insoluble |
| arsenic | 50 | 10 - 220<br>(2200)*<br>(< 50) | 14 6 ($As_2O_3$). (LD min of $As_2O_3$ = 1.43 for humans)(!) | 5.5 (As) |
| chromium | 50 | 13 - 220 (< 50) | 1870 ($CrCl_2$)(!) | 791 (Cr) |
| nickel | 50 | 3 - 308 (< 50) | 175 ($NiCl_2,6H_2O$)(!) | 43 (Ni) |
| lead | 50 | 5 - 627 (< 25) | 1500 ($PbCl_2$)(!) for cobaye | 1117 (Pb) |
| beryllium | ? | (< 25) | carcinogenic(!)(▮) | |
| vanadium | ~ 10 | 1 - 210 (2100)*<br>(< 50) | 350 ($VCl_3$)(!) | 113 (V) |
| cyanide | 50 | (< 40) | 485 ($C_3Cl_3N_3$)(!) | 68 (CN) |
| pesticides | 0,5 | - | 25 mg to few g/kg(+) | |
| weedkiller (Paraquat) | | | 157 and (35 - 45 for human)(+) | |
| aromatic polycyclic hydro-carbons | 0,2 | (< 0.09) (**) | 930 (benzene)(!)<br>5000 (toluene)(!)<br>490 (naphtalene)(!)<br>700 (phenantrene)(!)<br>2700 (pyrene)(!) | |

The (OJEC) has set the maximum contents of undesirable specks in drinking water. Table *2* lists respectively the maximum permissible contents of these undesirable species in drinking water, their minimum and maximum contents in the Dogger waters of the Park Basin, and their LD 50. As for the toxic species, we have observed the lethal doses of their soluble salt and recalculated LD 50 for the simple *species*. Data on humans have also been added

The maximum contents of cenain metals (Fe, Mn, Cu) should be attributed io the recent cleaning of the wells, the samples often being taken just after flow has resumed, but the maximum contents usually determined are lower. As for the toxic species, these high cntents nevertheless reveal the risk of greater pollution in the case of perforation during a cleaning operation.

A significant difference in tolerance is again observed between the rat and the human being. The LD 50 of phenol for man is about 45 times greater than that *fir* the rat, but it seems to be lower or approximately the same (unly LD min is available for humans] in the case of barium.

Overall chemistry of Dogger waters

In previous work (Abou Akar, 1994), we listed the contents of chemical spies of drinking water as defined in the OJEC. We added those of a number of Dogger waters characteristic of the main areas of genthennal exploitation (Rojas *et al.*, 1989). Characteristic of freshwater aquifers have also been added Table *3* shows the ratios between the average concentrations nf the Dogger waters arid those of drinking water or freshwater aquifers. An examination of these data shows that, fur nearly all the species assayed. the concentration in Dogger waters is significantly greater than its

Table 2. Undesirable **species.** maximum **permissible concentrations** in drinking water: **concentrations** in Dogger **water and** lethal **doses.**
values **between parentheses correspond** to recent sampling **carried** out on two wells (north and south of Paris). the **others correspond to** older analyses.
(*) after cleaning **the well.**
(!) : Merck catalogue 1992/93) (+) Encyclopédie Médico-chirurgicale

| chemical **species** | max. permissible concentration (µg/l) (OJEC) | concentration in Dogger Waters (µg/l) | LD 50 (mg/kg of rat)(!) | LD 50 (mg/kg of rat)(!) | DL 50 (mg/kg humans) |
|---|---|---|---|---|---|
| iron | 200 | 200 - 3000 (17000)* | 984 ($FeCl_2,4H_2O$) | 276 (Fe) | 250 ($FeSO_4$)(+) |
| manganese | 50 | 15 (1000)* (< 25) | 1715 ($MnCl_2$) | 749 (Mn) | |
| copper | 3000 | 13 - 1300 (< 50) | 300 ($CuSO_4$) | 119 (Cu) | |
| zinc | 5000 | 33 - 55 (< 25) | 350 ($ZnCl_2$) | 168 (Zn) | |
| **cobalt** | < 50 | < 220 (< 50) | 80 ($CoCl_2$) | 36 (Co) | |
| barium | 100 | 40 - 400<br>(184 - 266) | 118 ($BaCl_2$)<br>418 ($BaCO_3$)(+) | 78 (Ba)<br>291 (Ba)(+) | DL min -- 11 4 ($BaCl_2$)(+)<br>17 ($BaCO_3$)(+) |
| silver | 10 | < 55 (< 25) | 50 ($AgNO_3$) (mouse)<br>800 ($AgNO_3$) (DL min for rabbit) | 32 (Ag)<br>508 (Ag) | |
| nitrates | 50000 | < 500 | 3236 ($NaNO_3$) | 2360 ($NO_3$) | |
| nitrites | 100 | | 85 ($NaNO_2$) | 57 ($NO_2$) | |
| ammonium | 500 | 20 - 27 | 1650 ($NH_4Cl$) | 556 ($NH_4$) | |
| **boron** | 1000 | 6300 - 17600 | 650 (B insoluble) | 650 (B) | |
| phosphorus ($P_2O_5$) | 5000 | 5 - 627 | | | |
| fluorine 8-12 °C | 1500 | 4200 - 5700 | 52 (NaF) | 24 (F) | |
| 25 30 °C | 700 | | | | |
| nitrogen | 1000 | | | | |
| **hydrogen sulphide** dissolved | ~ 0 | 2000 - 90000 | | | |
| hydrocarbons | 10 | < 75000 | 28710 ($C_6H_{14}$) | | |
| phenols | 0,5 | 30 - 270 | 317 | | 14000(!) |
| organochlorined | 0,5 | | 570 (3-Chloro-phenol)<br>500 - 1000 (o- and m-dichloro-benzene)<br>10000 (p-dichloro-benzene) | | |
| surface agents | 200 | 2000 - 10000 | 2000 | | |

Table 3 - **Ratios** between the average concentrations of the Dogger **waters and** those of drinking water and freshwater aquifers.
*PAH* : Polycyclic **Aromatic** Hydrocarbons ; *DH* **Dissolved Hydrocarbons**; *SA* : **Surface Agents** ; CN Cyanide ; max perm conc maximum permissible concentration

| Major species | Cl | Na | Ca | Mg | K | $SO_4$ | $SiO_2$ | Al | $HCO_3$ | $O_2$ |
|---|---|---|---|---|---|---|---|---|---|---|
| [Dogger]/[max. perm. conc.] | 54 | 39 | 4 7 | 4 4 | 3.5 | 3.5 | 2.4 | 1.1 | - | - |
| [Dogger]/[guide level] | 433 | 293 | 9.4 | 7.3 | 8.8 | 35 | 7.1 | 4.5 | 30 | 0.001 |
| [Dogger]/[freshwater aquifer] | 470 | 560 | 12 | 32 | 13 | 36 | 3 5 | 11 | 1.5 | 0.01 |

| Undesirable species | D.H. | Phenol | $H_2S$ | $NH_4$ | B | Fe | S.A. | Mn | Co | Cu | Zn | $PO_4$ | $NO_3$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| [Dogger]/[max. perm. conc.] | 440 | 300 | 78 | 41.1 | 12 | 5.5 | 10 | 1.1 | 1 | 0.5 | 0.3 | 0.05 | 0.01 |
| [Dogger]/[freshwater aquifer] | 14600 | 7500 | 40 | 308 | 257 | 18 | 140 | 0.5 | 50 | 3 | 0.7 | 3.4 | 0.015 |

| Toxic species | Be | Cd | Sb | V | Hg | Se | As | Ni | Cr | CN | Pb | P.A.H |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| [Dogger]/[max perm. conc.] | 5 | 5 | 5 | 5 | 3 | 2.5 | 1 | 1 | 1 | 0.8 | 0 5 | 0.45 |
| [Dogger]/[freshwater aquifer] | 5000 | 27 | 2500 | - | 75 | 4.3 | 8.6 | 2.5 | 38 | 3.2 | 2 4 | - |

allowable concentration for drinking **water** These ratios are highest for $Na^+$, $NH_4^+$, $Cl^-$, $H_2S$, phenols and dissolved hydrocarbons. Note that concentrations **of dissolved** hydrocarbons in the **geothermal** fluid only concern gaseous **alkanes.** $CH_4$ to $C_6H_{14}$ expressed as **dissolved** gas. The ratios of the toxic **species** are lower, and in some cases, drop **below** 1. **However.** the **data** concerning **toxic** metals **must** be considered with caution, because of disparities between the few assays at our **disposal.** The tolerated percentages **of Dogger water in** freshwater aquifers were calculated and will be discussed in section 4.1.

The *data for dissolved* **hydrocarbons** *indicated* the **highest** ratios [geothermal water/freshwater]. Therefore, it **will be** interesting to discuss their biodegradability in **water** The Circular of the European Community in fact **classes** linear **hydrocarbons** as well as phenols and organo-chlorinated compounds among the undesirable species.

Barker *et al.*, (1987) investigated the natural attenuation of **aromatic** hydrocarbons **in water. The study was conducted in** the **laboratory** on groundwaters and in shallow **sandy** aquifers. It **included** benzene, toluene and the **ortho,** meta and para-xylene Laboratory experiments were performed in three different media, **aerated, slightly aerated** and purged by nitrogen. **The** hydrocarbons were dissolved *in* methanol, and their total concentration ranged from - 0 3 mg/l to 26 mg/l. In the **field** experiment, 1800 litres of a groundwater previously contaminated with **a mixture of** these aromatic **hydrocarbons** (about 9 mg/l) **was** injected into an uncontaminated **aquifer.** *A piezometer* array *monitored* the *migration* of the polluted bubble in the underground aquifer.

The results of Barker's **study** can be **summarized** as follows.

- Weight **losses** in aerobic medium were due to bioconversion of **the** hydrocarbons
- Nitrates **and** sulphates **present** in the **water did** not **appear to** participate **in** this bioconversion.
- The bioconversion of **benzene was the** slowest, **but diffusion of** $O_2$ in **the** water is the dominant **parameter** controlling **the** reaction.
- The total bioconversion time was 78 days, after **which** the hydrocarbon **concentrations** fell below **the** detection limit.
- In anaerobic medium, **an** initial bioconversion occurs **due** to residual **oxygen,** followed by stabilizing **of the** concentrations. The addition of **an** oxidant (nitrates) reinitiates the **bioconversion.**

The experiment conducted in the aquifer used **chloride** ions ($Cl^-$) as tracers **to illustrate the** dispersion effects. **Their mass** remained *reasonably constant. These ions nevertheless* **migrated** faster **than** the **hydrocarbons** due **to the** retarding **effect of adsorption of** the hydrocarbons. The study **yielded** results similar to **those** obtained in **the laboratory** in aerobic medium. Only **benzene** was still detected **after** 270 days, and **for** as **long** as 434 days. The absence of non-biological **reactions and irreversible adsorption, together** with the **laboratory** experiments, **makes** it possible to **attribute** the hydrocarbon **weight** losses to **their bioconversion.**

**Barker's** study followed a study **by** Sutton and Barker (1985) on the migration **and** attenuation *of* **certain organic species** (including **phenol and** para-chlorophenol) *in* sandy **aquifers.** The ***results of*** these **two studies are** in agreement.

These experiments are not unique in their field. Books dealing with underground aquifers and catchment protection zones mention the biodegradation of organic matter and explain it by the purifying power of the soil. This power is exerted in two ways:

- Nitrification, consisting of all the mechanisms which culminate in the conversion of the initial organic matter to soluble nitrates: fractured and limestone formations have a high nitrifying power (NP), while lower-lime siliceous soils have a low NP,
- Natural filtration, which arrests the microbes conveyed by the organic matter: this is a consequence of the interlocking of the grains of the impermeable formation, and this purification process is based on an adsorption mechanism.

In conclusion, the freshwater aquifers would be undrinkable if mixed with more than about 1.5 % of Dogger water. It is nevertheless important to state that

- the species most indicative of the intrusion of Dogger water are not the toxic species (e.g NaCl, that is recognizable by its taste),
- with an increasing percentage of Dogger water. the tolerable limit of NaCl is reached before that of the toxic species for which analyses are available.

It should also be noted that, while the tolerated percentage of dissolved hydrocarbons in Uogger water is very low, this does not account for their degradation by the purifying power of the soil

In another study on the methodology for detecting perforations in the casing of a geothermal well (Abou Akar *et al.*, 1994; 1995), we will see that some of these indicative species ($Na^+$, $Cl^-$) could play the role of a tracer to detect any infiltration of Dogger water into one of the freshwater aquifers (or *vice versa*).

### 5.2 Bacterial presence in Dogger waters, toxicity resulting from contamination of freshwater aquifers

The bacteria normally present in geothermal fluid are divided into eight categories (Daumas *et al.*, 1985a and 1985b):

- mesophilic aerobic heterotrophic microflora,
- thermophilic aerobic heterotrophic microflora,
- mesophilic anaerobic heterotrophic microflora,
- thermophilic anaerobic heterotrophic microflora,
- mesophilic sulphate-reducing microflora,
- thermophilic sulphate-reducing microflora,
- mesophilic methanogenic microflora,
- thermophilic methanogenic microflora.

The sulphate-reducing bacteria (SRB) belong to the group of the mesophilic sulphate-reducing microflora, and are anaerobic. Hartemann (1984) classed the bacteria into two categories:

- those exerting (or liable to exert) an effect on health,
- those responsible for corrosion, giving rise to the unpleasant aspects of the water.

SRB fall in the second category By participating in the corrosion of metals (Fe, Cu), they increase the concentration of these metals in the geothermal water. Any mixture with fresh water can impart a colour and a bad taste to the resulting mixture.

Despite the dissolved oxygen present in pipes carrying water intended for consumption, the presence of SRR in these pipes has been described by Lee *et al.*, (1980). The authors investigated the biological corrosion of freshwater supply circuits, but without being able to examine the extent and nature of their implication in pipeline corrosion. The mechanisms and the different aspects of anaerobic biological corrosion have nevertheless been studied and reviewed by Davis (1967). Iverson (1974), and Miller and Tiller (1970). Various studies show that microorganisms in water supply networks are associated with the sediments on the pipes and not with the water

Lewis (1965) attributed the rust and unpleasant odours present in drinking water to SRB. Quoting the work of Updegraff (1955) which established that chlorination was ineffective for the treatment of water against anaerobic bacteria due to the deactivation of the chlorine by the sulphide produced by these bacteria, he declared that this was only true in tubercles which contained a high accumulation of these sulphides. El-Zanfali *et al.*, (1986) agreed with Lewis on this additional detail For Lewis, chlorine, which can destroy individual cells, is effective against the formation of tubercles, and hence offers a good means of prevention However, if the tubercles have already formed, other means are needed to eliminate them before applying preventive treatment by chlorine.

Tuovinen *et al.*, (1980) analyzed scale collected in the water supply systems of Ohio, and found that the scale contained a variety of organisms including SRB These SRB are located inside the tubercles making up the scale (a reducing medium which is favourable to them). Corrosion and scaling processes similar to those which occur in geothermal casings take place inside these tubercles, The tubercles sampled proved to be rich in chlorine and sulphides, the latter resulting from the reduction of the sulphates. Note also that these microorganisms present in the tubercles are sheltered from the residual chlorine in the water However. this sheltering of the chlorine does not appear to concern the bacteria considered pathogenic for humans.

It is important to consider the potential 'side effects' of anti-bacterial treatment for quaternary ammoniums (QA. §3.3), and to mention as an example the work of Ventullo and Larson (1986) The authors analyzed the adaptation of heterotrophic aquatic bacteria to QA (mono and di-alkyl substituted). In general, none of the surfactants tested had any significant effect on the reduction of the bacterial density. Chronic exposure (21 days) of these bacteria to one of these QA enables them to recover their initial heterotrophic activity and also allows an increase in the number and activity of the bacteria capable of biodegrading the material entering into contact with these bacteria. This stud! showed that. in general, exposure of the microbial communities to QA allows the development of a community adapted to bactericides, which further degrade the contact material However, the species which adapted is not a SRB.

To conclude, SRB are incapable of developing in waters containing oxygen. However, they may survive (or even develop) in deposits adhering to piping in which oxygen diffuses with difficulty Their removal in a mixture of fresh water and geothermal water should not raise insurmountable problems, and could take place at the same time as the anti-bacterial treatment and the filtration of the water intended for human consumption. But it is important to remember that the bacteria present in biofilms and beneath scale can elude the different fluid treatments We are not able at present to assess the toxicity of the other types of bacterium present in the geothermal waters of the Pans Basin, mentioned above.

### 3.3 Treatment additives and their breakdown products

Treatment additives (surfactants) added to geothermal water, which contain bactericides and inhibitors of corrosion and crystal growth, have an LD 50 of about 2 g/kg of rat. Thus any toxicity analysis of the Dogger waters must take account of the presence of these additives and the dangers they incur for the health of living beings. For instance, the LD 50 of mercury and arsenic (toxic species). of iron and nitrates (undesirable species] dissolved in the water are respectively 0.74, 5.5, 276 and *2360* mg/kg of rat. A comparison of *these* values helps to class these additives among the undesirable species. The bactericidal agent in these additives is an alkyl-dimethyl-benzyl-ammonium salt (QA) also called benzalkonium salt:

$$[R - N(CH_3)_2 - CH_2 - C_6H_5]^+ , Cl^- \qquad (R = C_8H_{18} \text{ to } C_{18}H_{38})$$

The lauryl-dimethyl-benzyl-ammonium salt is used as bactericide against *Escherichia coli, Staphylococcus aureus* etc present in swimming pool water. These benzalkonium salts are also used in the food industry as cleaning agents and disinfectants, in the pharmaceutical and cosmetic industries, and in veterinary medicine

Note that the concentration of these chemical additives at the production wellhead is about 2 to 3 mg/l, and that Solamine 129 (one of the treatment additives routinely used in the treatment of the geothermal wells in the Pans Basin) contains about 66% of QA salt These substances are nevertheless degradable, and a complete study of their toxicity should take account of the toxicity of their breakdown products.

Studies on the toxicity of cationic surfactants are commonly based on their effects on the aquatic fauna, the primary victim of industrial and other releases into the rivers and lakes. Lewis and Wee (1983) investigated the effect of the addition of a quaternary ammonium salt on the mortality of fish and crustaceans. The waters tested were taken from rivers and wells, or reconstituted in the laboratory, and the quaternary salts examined were chlorides and methyl sulphates of dimethyl-dialkyl ammonium (with the alkyl radicals containing 15 or 17 carbon atoms).

The results of this study showed that the lethal concentration LC 50 [defined by analogy with LD 50 but per unit of volume of the water because it concerns the aquatic fauna) range from a few tenths of an milligram to a few milligrams of active species per litre of water, and was approximately the same as. or less than. the concentration of corrosion inhibitor in the geothermal water

Isomaa *et al.*, (1976) investigated the chronic toxicity of a cationic surfactant (cetyl trimethyl ammonium bromide) on populations of rats This study revealed that a dose of 20 mg/kg/day was well tolerated by their organisms. A dose of 45 mg/kg/day caused a weight loss in the population concerned. The geothermal water contains an average of 2 to 3 mg/l of surfactant. At equivalent toxicity between this additive and the one mentioned in the study. any freshwater/geothermal water mixture would not supply this daily toxic intake.

Balcux and Caumette (1977) studied the biodegradation of a number of cationic surfactants in sewage and river waters. Ten QA were tested in this way: three with linear chains. five with cyclic chains, nitrogen itself forming part of the cyclic chain (pyridine) or having only a benzyl radical (benzalkonium), as well as two cationic surfactants derived from petroleum

The results of this study can be summarized as follows.

- Linear chains are rapidly degradable (3 to 28 days).
- Presence of an aromatic ring generally prevents biodegradation. and the same applies to the presence of a branched fat chain (or both simultaneously).

The surfactants used to treat the Dogger waters are dimethyl-alkyl-benzyl-ammoniums. They are therefore similar to the one tested above. which nevertheless has a more branched structure, and which remains intact after 28 days. The stability of the latter is probably due to its structure, which, by a steric effect, protects it against any external attack. This appears to be the case when the overall results of this study are considered In consequence, the treatment additives break down easily because of their simplified structure

## 4. CLASSIFICATION BY DECREASING TOXICITY OF THE ELEMENTS PRESENT IN DOGGER WATERS

### 4.1 Chemical species

The classification of the species by decreasing toxicity was based on:

- the tolerated percentages of Dogger water in freshwater aquifers mentioned in section 3:
- the classification of the chemical species as major. toxic and undesirable.

Owing to their depth, the Dogger waters are normally free of the pathogenic organisms listed above, and which are often associated with the presence of man However, assuming that some of these germs could have reached the Dogger reservoir, the warm, anaerobic and reducing environment would arrest the development of many of them. Furthermore, the surface treatment applied to the water intended for human consumption serves to strip the fluid stream of the possible presence of these bacteria or of their remains. but the problem of their presence beneath the biofilms on the pipeline walls will continue to arise.

The tolerated percentages of Dogger water in freshwater aquifers were calculated from the mean concentrations of the species in these waters and the maximum permissible concentrations in drinking water. These percentages can be assembled in several groups as shown in Table 4. $Na^+$, $NH_4^+$, $Cl^-$. $H_2S$, phenols and dissolved hydrocarbons lead to the lowest tolerated percentages (around 2 % of Dogger water in the freshwater aquifers). Hence they are the first indicators of any pollution of these aquifer waters. None of these indicators is included in the species considered toxic. Note that some ratios (Dogger water/drinking water) and percentages could not be calculated or were estimated in the absence of data on the corresponding species (beryllium and vanadium) Vanadium is also undetermined in the freshwater aquifers. so two maximum and minimum values have been selected to be tested. Note also that, for toxic species, and certain undesirable species- the concentration taken into account is a maximum concentration which corresponds to the lower detection limit of the species in a charged water such as in the Dogger aquifer (the salinity of this water prevents reaching the lower limits of detection given for fresh waters)

Table 4 - Tolerated percentages of Dogger water in freshwater aquifers according to species concerned.
*PAH* : Polycyclic Aromatic Hydrocarbons , *DH* : Dissolved Hydrocarbons, *SA* . Surface Agents , CN : Cyanide.
The column "10-20%" (for example) indicates that the maximum tolerable percentage of Dogger water in the fresh water (relative to the species concerned) is greater than 10% but less than 20%. The column "0-100%" includes species which have an average concentration in Dogger water less than the average concentration in freshwater

| | unknown percentages | < 5% | 5 - 10% | 10 - 20% | 20 - 50% | 0 - 100% |
|---|---|---|---|---|---|---|
| toxic species | | | | Be, Cd, Sb, Se, V | Hg | As, Cr. Ni, Pb, CN, *PAH* |
| undesirable species | $NO_2$, $Cl_{residual}$ | $NH_4$, $H_2S$, *DH*, phenols | B, F, *SA* | Fe | Ag, | Co, Cu, Mn. $NO_3$, $PO_4$. Zn |
| major species | | Na, Cl | K | Ca, Mg. Ba, $SiO_2$ | $SiO_2$, $SO_4$ | Al, $O_2$, $CO_2$, $HCO_3$ |

An examination of these columns helps to establish a classification by decreasing toxicity from left to right and from the top down Thus beryllium (Be), cadmium (Cd), antimony (Sb), selenium (Se) and vanadium (V) appear to be the most toxic and are followed by mercury (Hg). Arsenic (As), chromium (Cr), nickel (Ni), *lead* (Pb). cyanides (CY) and PAH appear to be "non toxic" because they are present in the Dogger waters in contents lower than those tolerated in drinking water. Nor is it necessary to consider the lethal doses of the toxic and undesirable species, because they have already been used to set the maximum contents authorized by the European Communities. It must also be pointed out that a proportionality does not necessarily exist between the maximum contents authorized for humans and LD 50 for the rat. The LD 50 of mercury is about 400 times lower than that of antimony, although ten times less mercury than antimony is tolerated in drinking water. Among the species considered undesirable. the least tolerated are organic (hydrocarbons and phenols), whereas heavy metals are tolerated in much higher percentages in Dogger water. The carbon species $CO_2/HCO_3^-$ appear in the column "0 - 100 %" The maximum alkalinity tolerated is not indicated in the European Directive. but the average alkalinity of the Dogger waters (about 400 mg/l) remains lower than that of certain mineral waters (around 450 mg/l).

This classification is nevertheless offered for guidance only, owing to the uncertainty in the various analyses that were supplied to us, and the fact that the figures are average or maximum contents determined.

### 4.2 Bacteria and treatment additives

The literature review in Section 3 showed that sulphate-reducing bacteria (in the conditions in which they are found) incur no direct danger for human health This study also revealed that this type of bacteria in pipes at the surface is able to live in the biofilms and the deposits on the pipelines (oxygen-poor areas). to elude the treatment additives, and to promote the production of sulphides. thus favouring iron corrosion This gives rise to the risk of perforation, the formation of iron sulphide scale on the pipe walls: and an increase in the contents of iron and dissolved sulphides, species judged undesirable in drinking water supply networks.

The treatment additives (in the concentrations employed) also appear to incur no direct danger for human health. In fact, surfactants are tolerated in the human body up to contents substantially exceeding their content used in the Dogger waters. For reasons of confidentiality, the exact formulas of the surfactants used in the treatment additives are not disclosed by the manufacturers, but these agents (or at least most of them) have structures that facilitate their breakdown

## 5. CONCLUSION

This study has served to evaluate the toxicity of Dogger waters and to compile a preliminary comparison between these waters and those of freshwater aquifers. The consequences of the pollution of these aquifers by the Dogger water have accordingly been assessed $Na^+$, $NH_4^+$, $Cl^-$, $H_2S$, phenols and dissolved hydrocarbons lead to the lowest tolerated percentages (around 2 %) of Dogger water in the freshwater aquifers) Hence they are the first indicators of any pollution of these aquifer waters but none of these indicators is included in the species considered toxic The gustatory manifestation of such pollution would be an increase of the sodium chloride (NaCl) content of the fresh water, a species considered neither toxic nor undesirable In fact. Dogger water is about 500 times richer in chloride ($Cl^-$) and sodium ($Na^+$) than the freshwater aquifers, whose $Cl^-$ and $Na^+$ contents are close to those of the guide level for drinking water The greatest risk by order of increasing percentage of Dogger water in the freshwater aquifers stems from the non-metals and particularly from sulphides and dissolved hydrocarbons. classed among the undesirable species. It is in higher percentages (around 10 %) that the first toxic metals engender their effects, the most toxic being antimony, cadmium, selenium, beryllium, vanadium and mercury. The sulphate-reducing bacteria present in geothermal water and the additives used to treat this water (in the concentrations employed) do not incur any direct danger for human consumption. It is nevertheless important to consider the possibility that these bacteria could continue their activity despite the anaerobic medium considered hostile to their development. The toxicity of the other bacteria present in the geothermal water could not be dealt with due the lack of pertinent data.

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## 6. REFERENCES

Abou Akar A. (1994). *Risque de pollution des nappes d'eau douce du fait des exploitations géothermales de l'aquifère du Dogger du Bassin parisien. 1. Evaluation de la nocivité des eaux du Dogger.* Rap. BRGM R 38032 GGP-DR-94, 87pp.

Abou Akar A. and Lafforgue M. (1994). *Etude de la corrosion par coupons en acier au carbone placés en zones monophasique et diphasique sur la centrale géothermique de Chelles (Seine-et-Marne).* Rap. BRGM R 37832 GGP-DR-94, 91pp.

Abou Akar A., Ignatiadis I., Lesueur H. and Longin G. (1994). *Risque de pollution des nappes d'eau douce du fait des exploitations géothermales de l'aquifère du Dogger du Bassin parisien : 4. Méthodologie de détection des percements intervenus sur le tubage d'un puits géothermique.* Rap. BRGM R 38035 GGP-DR-94, 47pp.

Abou Akar A., Ignatiadis I. and Lesueur H (1995). Methods for detecting perforations in casings of wells exploiting geothermal fluids. *In this volume.*

Baleux B. and Caumette P. (1977). Biodégradation de quelques agents de surface cationiques. *Water Research*, vol. 11 (9), pp. 833-841.

Barker J.F., Patrick G.C. and Major D. (1987). Natural attenuation of aromatic hydrocarbons in a shallow sand aquifer. *GWMR*, vol. 7 (1), pp. 64-71.

Boisdet A., Bray Ph., Ignatiadis I. and Abou Akar A. (1992). *Study of corrosion and scaling in low enthalpy geothermal systems.* Rap. final IMRG du contrat CCE Joug-0005-C. Rap. BRGM R36103 IRG SGN 92, 312pp.

Casarett & Doull's (1991). *Toxicology, the basic science of poisons*, Mc Graw- Hill, 4th.

Daumas S., Goyeneche O. and Bianchi A. (1985a). Bactériologie : Activites métaboliques des bactéries des eaux géothermales du Dogger et du Trias du Bassin parisien. *C.R. Acad. Sc. Paris*, t. 301, serie III, n° 6, pp. 295-297.

Daumas S., Lombart R. and Bianchi A. (1985b). A bacteriological study of geothermal spring waters dating from the Dogger and Trias period in the Paris basin. *Geomicrobiology Journal*, vol. 4 (4), pp 423-433.

DAVIS J.B. (1967). *Petroleum Microbiology.* Elsevier Publ. Co., New York.

Dupont A. (1986). *Hydraulique urbaine, t. 1, Hydrologie. Captage et traitement des eaux.* Ed. Eyrolles, 262pp.

El-Zanfaly H.T., Kassim E.A. and Hassan H.M. (1986). The effect of selected biocides on sulfate-reducing bacteria. *Toxicity assessment : An International Quaternly*, vol. 1 (4), pp. 455-464

Encyclopédie Médico-chirurgicale. Editions techniques Paris, directeur de publication : Ph. DURIEUX.

Hartemann Ph. (1984). L'eau et les bactéries dans les canalisations. *Mét. Corr. Indus.*, vol. 59, n° 707-708, pp. 246-251.

Honneger J.-L. *et al* (1986) *Expertise dans le domaine de la corrosion et optimisation des matériaux de l'exploitation géothermique.* Rap. annuel BRGM/IMRG 1986.

Honneger J.-L., Traineau H., Criaud A. and Samson S. (1989). *Comportement des matériaux métalliques en environnement géothermal basse enthalpie, Bassin parisien, France.* Rapport final CONTRACT EN3G-0038F. Rap. BRGM 89 SGN 625 IRG, 138pp

Ignatiadis I., Cheradame J.M., Lafforgue M. and Castagne S. (1991). *Evolution des concentrations en sulfures dissous dans les fluides géothermaux du Dogger du bassin de Paris.* Rap. BRGM R 33518 IRG SGN 91, 134pp.

Ignatiadis I. (1994). Origins of the increased sulphide concentrations noted in geothermal fluids at production wellheads in the south and east of the Paris Basin. *In:* Proceeding of the International Symposium, Geothermics 94 in Europe, from Research to Development, BRGM (ed), Orléans, France, 8-9 February 1994, pp. 241-248.

Isomaa B., Reuter J. and Djupsund B.M. (1976). The subacute and chronic toxicity of cetyl-trimethyl-ammonium bromide (CTAB), a cationic surfactant, in the rat. *Arch. Toxicol.*, vol. 35 (2), pp. 91-96

Iverson W.P. (1974). *Microbial corrosion of iron. Microbial iron metabolism.* Academic Press, Inc., San Francisco, California.

Lee S.H., O'connor J.T. and Banerji S.K. (1980). Biologically mediated corrosion and its effects on water quality in distribution systems. *Research and Technology, Journ. AWWA*, pp. 636-645.

Lewis M.A. and Wee V.T. (1983). Aquatic safety assessment for cationic surfactants. *Environmental Toxicology and Chemistry*, vol. 2, pp. 105-118.

Lewis R.F. (1965). Control of sulfate-reducing bacteria. *Jour. AWWA*, vol. 57 (8), pp. 1011-1015.

Merck catalogue (1992/1993) *Réactifs, Diagnostica, Produits chimiques*, 1558pp.

Miller J.D.A. and Tiller A.K. (1970). *Microbial corrosion of buried and immersed metal. Microbial aspects of metallurgy*, (J.D.A. Miller editor), American Elsevier Publ. Co., New York.

OJEC (1980). Directive de conseil du 15 juillet 1980 relative à la qualité des eaux destinées à la consommation humaine. *Journal officiel des Communautés européenes*, 30 août 1980, n° L 229, pp. 11-29.

Rojas J., Giot D., Le Nindre Y.-M., Criaud A., Fouillac Ch., Brach M., Menjoz A., Martin J.-C., Lambert M., Chiles J.-P., Fouillac A.M. and Pauwels H., (1989). *Caractérisation et modélisation du réservoir géothermique du Dogger, Bassin parisien, France, rapport final.* Rap. BRGM R 30169 IRG SGN 89, 249pp.

Sutton P.A. and Barker J.F. (1985). Migration and attenuation of selected organics in a sandy aquifer A natural gradient experiment. *Ground Water*, vol. 23 (1), pp. 10-16.

Tuovinen O.H., Button K.S., Vuorinen A., Carlson L., Mair D.M., and Yut L.A. (1980). Bacterial, chemical and mineralogical characteristics of tubercles in distribution pipelines. *Research and Technology, Journ. AWWA*, pp. 626-635.

Updegraff D.M. (1955). Microbiological corrosion of iron and steel. *Corrosion*, 11, 442t.

Ventullo R.M. and Larson R.J. (1986). Adaptation of aquatic microbial communities to quaternary ammonium compounds. *Applied and environmental microbiology*, vol. 51 (2), pp. 356-361.