PROCEEDINGS, Thirteenth Workshop on Geothermal Reservoir Engineering
Stanford University, Stanford, California, January 19-21, 1988
SGP-TR-113

CHEMISTRY OF A LOW TEMPERATURE GEOTHERMAL RESERVOIR : THE TRIASSIC SANDSTONE AQUIFER AT MELLERAY, FRANCE.

François-David Vuataz, Christian Fouillac, Sylvie Detoc
and Michel Brach

Institut Mixte de Recherches Géothermiques
BRGM - BP 6009, 45060 ORLEANS CEDEX 2 - FRANCE

ABSTRACT

The Triassic sandstone aquifer offers on a regional scale, a large potential for low-temperature geothermal exploitation in the Paris Basin. The Na-Cl water in the aquifer has highly variable mineralization (TDS = 4 to 110 g/l) and a wide range of temperature (50° to >100°C). Chemical studies have been carried out on the Melleray site near Orléans, where a single well was producing a Na-Cl geothermal water (TDS = 35 g/l) at a wellhead temperature of 72°C to provide heat for greenhouses.

The purpose of these studies is to understand the chemical phenomena occurring in the geothermal loop and to determine the treatment of the fluid and the exploitation procedures necessary for proper reinjection conditions to be achieved. During the tests performed after the drilling operations, chemical variations in the fluid were noticed between several producing zones in the aquifer. Daily geochemical monitoring of the fluid was carried out during two periods of differing exploitation conditions, respectively pumping at 148 m^3/h and artesian flow at 36 m^3/h. Vertical heterogeneities of the aquifer can explain the variations observed for the high flowrate.

Filtration experiments revealed that the particle load varies with the discharge rate and that over 95 weight % of the particles are smaller than 1 μm. The chemistry of the particles varies greatly, according to their origin as corrosion products from the well casing, particles drawn out of the rock or minerals newly formed through water-rock reactions.

Finally, small-scale oxidation experiments were carried out on the geothermal fluid to observe the behaviour of Fe and SiO_2 and to favour particle aggregates for easier filtration or decantation processes.

INTRODUCTION

During the late 1970s, the sandstone aquifer in the Triassic of the Paris Basin was drilled for geothermal purposes. The first drillhole, at Cergy, west of Paris, gave insufficient yield. The two following operations at Melleray (near Orléans) and Achères (west of Paris), despite showing good reservoir productivity, gave poor performance on reinjection (Fig. 1). Solving these reinjection problems was the main task of a research program supported by the Commission of the European Communities (Fouillac et al., 1986).

The present paper summarizes a detailed study of the chemical aspects of the fluid and solid particles at the Melleray geothermal site carried out to acquire a comprehensive knowledge of the chemical interactions occurring between the fluid, the reservoir rock and the casing and tubing materials. The understanding of these phenomena is necessary for the future design of water treatment and reinjection procedures.

The chemical and hydrogeological information obtained from the wells penetrating the Triassic aquifer is much less than that available for the Dogger aquifer in the overlying Jurassic rocks (Rojas et al., 1987). Figure 1 shows the location of the wells on which fluid chemical data were obtained and shows the extension of the Triassic geothermal aquifer (> 10000 km^2). Three types of well have been considered :

- geothermal wells (Cergy, Melleray 1 and 2, Achères 1 and 2);
- wells drilled for potential gas storage (Romorantin, Chemery);
- oil exploration wells (Marchenoir, Pasnes, Blancafort, Etampes, Mantes, Chaunoy).

The fluids from the Triassic aquifer are characterized by a wide range of temperature (45° to 155°C) related to aquifer depths between 950 and 2440 m. The geothermal waters are of Na-Cl type with important amounts of Ca and SO_4. Their mineralization is also strongly variable with Total Dissolved Solids from 4 to 110 g/l, according to their location within the aquifer. As a general rule, the mineralization of the fluids increases with depth but the linear correlation between these two parameters is only fair. The amount of dissolved chemical species is of course related to the distance that the water circulates between the recharge zone and the wells, and also to the occurrence of soluble minerals such as evaporites leached by the groundwater.

Na exhibits a very good linear trend against Cl (Fig. 2) which could mean that neither element is controlled by secondary minerals. The slope of the linear curve is not compatible with halite being the source of both Na and Cl and therefore another mineral source for sodium (plagioclase ?) is needed (Fouillac et al., 1986).

At Melleray, near Orléans (120 km south of Paris) one production well (GMY1) and one injection well (GMY2) were drilled in 1980 to depths of respectively 1669 and 1661 m. The producing zones of the Triassic aquifer are equipped with slotted liners from about 1400 to 1600 m. Both wells are artesian and at the level of the reservoir are separated horizontally by 1000 m.

Saline water (TDS = 35 g/l) pumped from the production well GMY1 at 150 m^3/h with a wellhead temperature of 73°C, has been used intermittenly for several years to heat a complex of greenhouses. Due to great difficulties of reinjection, the geothermal water was discharged after cooling in the nearby Loire River.

VARIATIONS IN FLUID CHEMISTRY

During the first sampling carried out at Melleray at the end of drilling, variations of chemical composition were established related to the different producing layers of the Triassic reservoir. Physical and chemical monitoring of the fluid was therefore carried out to improve the knowledge of the geothermal fluid and its variations with time and space, and to draw up a program of treatment of the fluid with a view to reinjection.

Daily monitoring of the production well

Measurements and sampling were carried out at the GMY1 wellhead on a daily basis for two periods of about one month, corresponding to periods of differing production rates. Five days a week, water samples were collected and measurements of pressure, discharge rate, temperature and pH were made at the wellhead. The total alkalinity (HCO_3) was analyzed within the next few hours. To obtain maximum analytical precision and to avoid problems of drift, Fe, SiO_2 and Cl were analyzed only at the end of each survey on filtered (0.45 µm) and acidified water samples.

Table 1 shows that at the different discharge rates and pressures corresponding to the two survey periods, four of the six parameters compared display absolute variations. The temperature decreased by 3°C between the first and second surveys owing to decreasing fluid velocity in the well. The pH decreased by 0.23 units while HCO_3 increased by 13 mg/l. Fe increased by 13 mg/l. Fe increased notably, by 2.2 mg/l. Note that as the bubble-point pressure is very high (17-20 bars), the geothermal fluid was more degassed at 1.8 bars (2nd survey) than at 5 bars (1st survey).

Table 1 - Mean and standard deviation of parameters measured during the two daily survey periods of production well GMY1.

Parameters	1st survey mean ± stand. dev.	2nd survey mean ± stand. dev.
Flowrate (m^3/h)	148 (pumped)	36 (artes.)
Pressure (bars)[a]	5	1.8
Temperature (°C)[a]	72.4 ± 0.1	69.4 ± 0.3
pH[a]	6.30 ± 0.02	6.07 ± 0.01
HCO_3 (mg/l)	295 ± 5	308 ± 2
Fe "	7.9 ± 0.5	10.1 ± 0.1
SiO_2 "	37.4 ± 0.3	36.8 ± 0.3
Cl "	19520 ± 800	19870 ± 40
nb of measurements	30	25

[a] Wellhead measurements

In terms of time-variations, important differences have also been noted between the first and the second surveys. During the first (under pumping), the five chemical parameters, respectively pH, HCO_3, SiO_2, Fe and Cl show relatively large variations, cleary greater than the precision of the measurements (Fig. 3A). The variations of the different parameters are not always in phase and no repetitive events have been detected. On the 25th day, major variations were simultaneous for four parameters. During the second survey (artesian flowrate), the pH and the dissolved species vary only slightly with time but the variations remain very close to the limit of reproducibility of the measurements (Fig. 3B).

Several phenomena can tentatively be invoked to explain these variations :

1) Unstable pumping rate, contrary to the flowmeter indication (148 ± 2 m^3/h) ; electromagnetic flowmeters are often unprecise in two-phase flow.
2) Increase of fluid/casing interaction due to slower ascent during the second survey. For a total fluid volume of 84 m^3 and for discharge rates of 140 and 36 m^3/h, 36 min. and respectively 140 min. are needed for the fluid to reach the wellhead.
3) Further degassing for the second survey due to reduced pressure, with the result that the large amount of gas can create around each gas bubble an acidic water-gas emulsion, which intensely corrodes the casing.

4) Chemical variations as a function of discharge rates may be linked to production of different layers of the Triassic aquifer. Indeed, the lower pH of the second survey is in contrast to the more pronounced degassing when the loss of CO_2 should have increased the pH of the water at the wellhead. Variations in Cl also relatively important at 148 m^3/h, suggest heterogeneity of the fluids contained in the sandstone reservoir.

Variations of the fluid with depth and production rates

At the end of drilling in well GMY1 in 1980, two downhole samples (GMY1 80.1 and 80.2) were collected between packers at different depths. The concentration of major ions show important differences (Table 2) with TDS values of 32.4 g/l for the shallow sample (1441-1471 m) and 37.0 g/l for the deep one (1561-1593 m). Spinner surveys indicated that these two zones provide respectively 20 and 25 % of the total production in well GMY1. Such low and high TDS values have not been found for any subsequent samples collected at the wellhead and thus representing the average of all the producing layers of the Triassic aquifer (TDS = 35.0 to 35.8 g/l).

Finally, the vertical and possibly horizontal heterogeneity in fluid composition between the different producing layers seems to be confirmed by the sample collected at the wellhead of GMY2. For a similar discharge rate (85 m^3/h), the total mineralization of the fluid (34.7 g/l) is lower than that for GMY1 (35.3 g/l) (Table 2).

Table 2 - Chemical composition of selected samples of the geothermal fluid from wells GMY1 and GMY2, Melleray.

Samples	GMY2 1	(1) GMY1 1	(1) GMY1 2	GMY1 3	GMY1 4	GMY1 5	GMY1 30	GMY1 70
Month/Year	12/80	1/80	1/80	2/80	12/83	11/85	3/86	12/86
Flowrate m^3/h (2)	85	-	-	138	170	85	146	36
Temperature °C (3)	69	-	-	69.5	67	71	72.4	69.5
pH (3)	6.28	-	-	6.75	6.17	6.34	6.33	6.07
Na mg/l	10900	10760	11960	11680	11000	10880	11860	11700
K "	309	295	340	319	320	316	249	310
Ca "	1166	1132	1344	1236	1236	1210	1174	1200
Mg "	374	331	417	390	409	358	366	363
Cl "	19738	17572	20963	19312	20000	20280	19009	19808
SO_4 "	1800	1900	1550	1840	1760	1820	1890	1950
HCO_3 "	305	442	397	360	319	292	293	308
SiO_2 "	37	-	-	38	37	31	37.3	36.6
Fe "	-	-	-	36	6.1	9.7	7.2	10.2
Sr "	41.2	-	-	44.1	45.0	35.8	38.8	37.7
Li "	13.1	-	-	14.6	10.6	-	11.2	11.3
Ba "	$\leqslant 1$	-	-	-	0.26	0.165	0.176	0.154
B "	-	-	-	13	16.1	-	16.5	16.4
F "	-	-	-	1.4	1.3	4.3	3.5	2.8
Al "	-	-	-	-	0.030	0.332	0.638	0.451
TDS g/l	34.7	32.4	37.0	35.3	35.2	35.2	35.0	35.8
Sum cations meq/l	574	559	630	614	585	572	614	609
Sum anions meq/l	599	542	630	589	606	615	581	605

(1) Samples GMY1 1 and 2 were collected between packers between the depths of 1441-1471 m and 1561-1593 m respectively. All the other samples are from wellheads.

(2) Flowrates are pumping rates, with the exception of 36 m^3/h in 1986, which represents artesian discharge.

(3) Temperature and pH were measured at the wellheads.

Because the pH and HCO_3 measurements were not standardized, not all the parameters of fluid samples collected from the wellhead of GMY1 for various production rates over six years, can be readily compared. Fe content however increases as discharge falls, which confirms the evolution observed during the two daily surveys (Fig. 4). As mentioned before, both the time of contact between fluid and casing during ascent in the well and the degassing rate, parameters which are essential for corrosion phenomena, are highly variable.

PARTICLE DISTRIBUTION

Numerous filtration experiments have been carried out at Melleray, mainly on the wellhead of GMY1, using a small stainless steel filtration unit (filter area 1.73 x 10^{-3} m^2), which limited the volume of fluid filtered (1 to 40 x 10^{-3} m^3). The method was checked using a large filtration unit (filter area 0.36 m^2) and volumes of fluid (27 to 113 m^3). The particle load is very variable according to the production rate. Under pumping at 148 m^3/h, the total load of particles $\geqslant 0.01$ μm equals 4.8 mg/l, whereas for the artesian discharge (~ 36 m^3/h), the total amount of particles reaches 7.5 mg/l (Table 3). These values should be considered carefully because the particle load will be reinjected into the aquifer unless the fluid is treated by physical and/or chemical processes to remove the particles.

Table 3 - Particle load and weight, geothermal fluid at the GMY1 wellhead.

Flowrate (m^3/h)	Particle load $\geqslant 0.01$ μm (mg/l)	Total weight (kg/day)	ton/7 months[a]
148 (pumping)	4.8	17	3.6
~36 (artesian)	7.5	6.5	1.4

[a] Seven months is the length of a normal heating season.

Particle distribution as a function of size has been evaluated using values of the solid load obtained in filtration experiments during artesian discharge (36 m^3/h). It appears that more than 94 weight % of the particles are less than one micron in size and more than half is $\leqslant 0.1$ μm (Fig. 5). With the exception of the interval 0.2-0.45 μm, the particle distribution decreases logarithmically from small to large particles.

SCALING AND CORROSION PRODUCTS

In 1984, a mineralogical study of the particles contained in the geothermal fluid at the GMY1 wellhead showed the lack of amorphous phases (Boulmier, 1984). All the particles retained on the filter, even the finest, were more or less crystalline. Fe, a major element, occurred essentially as magnetite but also as sulphide, associated with Cu, and in phyllosilicates. Cu was relatively abundant but poorly crystallized (Cu + S, Cu + Fe + S). Zn and Pb were also detected. Free SiO_2 was seldom seen, but Si and Al were associated in kaolinite and illite. In some filter residues, the presence of gypsum, dolomite, quartz, marcasite and pirsonnite ($Na_2Ca(CO_3)_2 \cdot 2H_2O$) was detected by X-ray diffraction.

Two series of filter residues analyzed in 1986 for different production rates (150 and 36 m^3/h), differ considerably from each other as well as from the 1984 residue. The particle-size distribution is similar but an important amorphous phase of complex composition was found in the later filtration residues. The chemical nature of the particles is extremely varied (quartz, Fe sulphide, phyllosilicates, Fe oxides and hydroxides, complex carbonates, etc.), as is their size ($<$ 0.1 μm to $>$5 μm). On the other hand the amorphous phase is relatively homogeneous in composition, consisting essentially of Fe, with which is associated, in order of decreasing importance, Al, Si, S, P, Cl, Ca and Pb. For particles collected in the heating plant after cooling of the geothermal fluid, several elements were found in greater proportions in the amorphous phase, such as Cr, Pb, V, Ti and Zn. These are indicators of corrosion of the pipes and the heat exchanger in the heating plant.

Scaling products have been collected in the 200 μm protection filter of the plant. Their large particle size (0.1 to 1 cm), their platy shape and their composition (75-82 % Fe_2O_3) indicate their origin in the well casing and the pump suspension tubing. Magnetite, goethite and traces of siderite were the principal minerals found by X-ray diffraction.

Finally a series of filters of various sizes and qualities (Millipore, Sartorius, Nuclepore) and of different porosities (3, 1.2, 0.4 μm) was analyzed after deposition of particles from the artesian discharge of 36 m^3/h. Most particles are amorphous and remain undetected by X-ray diffraction. With the electron microscope an amorphous coating of S + Fe + Zn was found. In contrast of the previous residues, ZnS was a major phase, determined by microscopy as well as by chemical analysis with a Zn/Fe ratio ranging from 1 to 5. Cu and clay were also more abundant than in the earlier filtration residues.

The major variations observed with time consist in a progressive increase of the amorphous phase and the disappearance of Cu sulphide, replaced by Zn sulphide as the main particulate mineral phase in the geothermal fluid. Although no proof has yet been found, the abundant Zn could originate from either corrosion of the sampling port couplings or from the aquifer rock. As for sulphur, though it may exist in infra-trace quantities, it has not been detected in the fluid. Temporary occurrence of ZnS as a major amorphous phase could also be explained by "puffs" of fluid enriched in Zn, which mix with fluids from another productive zone containing S. In support of this suggestion, seven analyses of the geothermal fluid carried out between 1983 and 1986 for various producing conditions revealed high variations of Zn ($\leqslant$ 50 to 500 ppb), which shows the considerable changes in certain dissolved chemical species.

FLUID/MINERAL EQUILIBRIUM

Water/rock interactions have been approached using a computer code to determine which minerals exert a control on fluid chemistry under downhole conditions. The code WATRA2 (Sevèque et al., 1984) is a modified version of WATEQ F (Plummer et al., 1976). Prior to computing the degrees of saturation of the fluid in selected minerals, it was necessary to calculate independently the redox potential (Eh) and the pH value in the reservoir, as these two parameters are modified during the ascent of the fluid in the well due to slight conductive cooling and partial degassing.

The results of these computations show that the deep fluid is very close to equilibrium with carbonates, particularly with calcite, magnesite and siderite. Equilibrium is also attained to varying degrees for several SO_4-minerals, fluorite and chalcedony, whereas quartz was identified as the newly formed silica phase in the reservoir rock (Cautru and Robelin, 1984). The difficulty in computing equilibrium with H_4SiO_4 is due to the estimation of activity coefficients for this species, which could explain the discrepancies between calculations and observations.

With two input values for aluminum, the program indicates oversaturation of the solution with respect to kaolinite and illite, which have been positively identified (Cautru and Robelin, 1984). This places some doubt on either the accuracy of aluminum determinations or the reliability of the thermodynamic data set for aluminous species. The solution is also oversaturated with respect to K-feldspar, although secondary orthoclase was described in the Triassic sandstone. This suggests that the same comment is valid as for aluminum.

PRELIMINARY WORK ON FLUID TREATMENT

In order to establish a fluid treatment with a view to reinjection into the Triassic sandstone, several oxidation experiments have been carried out. Three oxidizers were tested: air, water saturated with dissolved O_2 and NaOCl. Only the last enables quantitative control of the oxidation of Fe^{2+} to Fe^{3+}. This can be induced very quickly and appears to involve about 5 % of SiO_2 during the precipitation of Fe^{3+}. The procedure allowed injection of a precise amount of NaOCl during the fluid treatment for an adjusted oxidation of 95 to 98 % of Fe^{2+} and thus avoided an excess of oxidizer, which would be corrosive toward the pipes of the geothermal loop. Other oxidizers will be tested to determine which will induce the coarsest aggregates, likely to be easily decanted and/or filtered.

If, during the treatment used for the reduction of Fe content, the geothermal fluid becomes slightly undersaturated toward minerals such as calcite, siderite and chalcedony, the reinjected fluid would tend of dissolve these minerals in the aquifer and increase or at least maintain the porosity around the reinjection well. Finally, complete degassing of the fluid would avoid the clogging of the pores by micro-bubbles of gas.

CONCLUSIONS

Comprehensive study of the geothermal fluids of the Triassic sandstone aquifer established that the producing zones are very heterogeneous at the scale of the Paris Basin, as well as at kilometer scale, between two boreholes or even between two producing layers in the same borehole. Consequently, the distribution of the slotted liners and the modification of the exploitation conditions for a given well (flowrate, pressure) can significantly change the fluid chemistry.

It is clear that the chemical variations of the fluid observed at Melleray during the two one-month survey periods are more important for the high than for the low flowrate. This is true even for non-reactive dissolved species such as Cl and supports the hypothesis of local vertical heterogeneity of fluid composition in different layers of the Triassic, as established from previous downhole sampling and differences between production and reinjection wells.

Filtration experiments showed that particles between 0.1 and 0.01 μm constitute more than 50 % of the total solid load and about 90 % of this is composed of particles $\leqslant$ 0.45 μm. The amount of particles is inversely proportional to the discharge rate of the well. At a flowrate of 150 m^3/h, 17 kg of residues enter the heating plant daily.

The chemical composition of these particles indicate different origins : Fe-oxides and hydroxides and traces of Cr and Ti represent mainly products of corrosion of the well casing. On the other hand elements such as Al, Si, S, Ca and Mg originate in the geological environment. The existence of a significant amorphous phase has been established but its composition varied with time. At first Fe was the major component (associated with S, Al, Si and Pb) but then ZnS became the most abundant phase.

The Melleray geothermal fluid is in chemical equilibrium with respect to calcite, siderite, magnesite fluorite and chalcedony, whereas the nature of the Al-limiting phase is still debatable. Problems of reinjection of the fluid into the Triassic sandstone have shown the necessity for treatment of the fluid. The study of the parameters which induce clogging of the rock matrix is underway, but possible steps in the fluid treatment can already be suggested, namely degassing, oxidation, decantation, filtration and injection of corrosion inhibitors.

ACKNOWLEDGEMENTS

This work was carried out under contract n° EN 3G-0006-F (CD) of the Commission of the European Communities and received financial support from the Bureau de Recherches Géologiques et Minières and the Agence Française pour la Maîtrise de l'Energie. The authors wish to thank all those in the BRGM who contributed to this phase of the project. Special thanks are due to Annie Criaud, IMRG, for her critical comments on the draft and to J. Kemp, BRGM, for improving the English of the final version. B. Gayet and J. Rabian, IMRG, are respectively thanked for drafting and typing.

REFERENCES

Boulmier J.L., 1984 - Exploitation des formations gréso-argileuses du Trias. Etude des particules en suspension dans l'eau du forage de Melleray (Loiret). BRGM report, 84 SGN 279 MGA, 16 p. (unpubl.).

Cautru J.P. and Robelin C., 1984 - Etude d'un réservoir argilo-gréseux. Cas du Trias du doublet géothermique de Melleray, Loiret. BRGM report 84 SGN 124 IRG-GEO, 34 p. (unpubl.).

Fouillac C., Vuataz F.D., Brach M. and Criaud A., 1988 - Water-rock reactions in a Triassic sandstone aquifer. Detailed study of a low temperature geothermal system, Melleray, France. European Community Contractors Meeting, Geochemistry, Antwerp, Nov. 1986, 12 p. (in press).

Institut Mixte de Recherches Géothermiques, 1987 - Exploitation géothermique des formations argilo-gréseuses : Trias. Rapport annuel d'activités 1986 (unpubl.).

Plummer L.N., Truesdell A.H. and Jones B.F., 1976 - WATEQ F. A Fortran IV version of WATEQ, a computer program for calculating chemical equilibrium of natural waters. U.S.G.S. WRI, 76-13, 61 p.

Rojas J., Menjoz A., Martin J.C., Criaud A. and Fouillac C., 1987 - Development and exploitation of low enthalpy geothermal systems : example of the Dogger in the Paris basin, France. 12th Workshop on Geothermal Reservoir Engineering, Stanford, 6 p.

Sevèque J.L., Oustrière P. and Criaud A., 1985 - WATRA 2, programme de calcul d'équilibre dans les eaux. Une version de WATRA étendue aux espèces métastables du soufre : polysulfures, thiosulfates et sulfites, données thermodynamiques révisées et complétées. BRGM report 85 SGN 061 GMX, 123 p. (unpubl.).

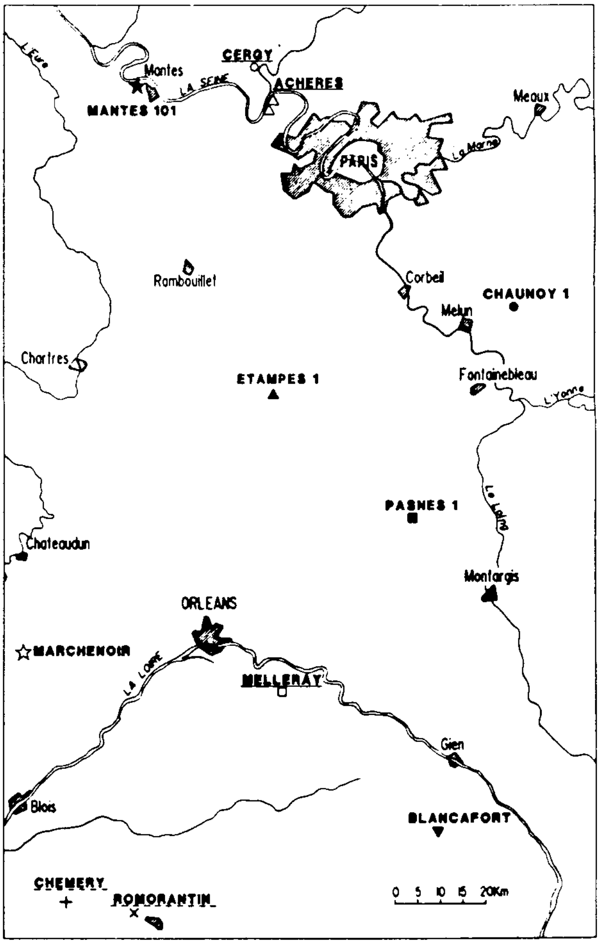


Fig. 1 - Location map of the wells on the Triassic sandstone aquifer.

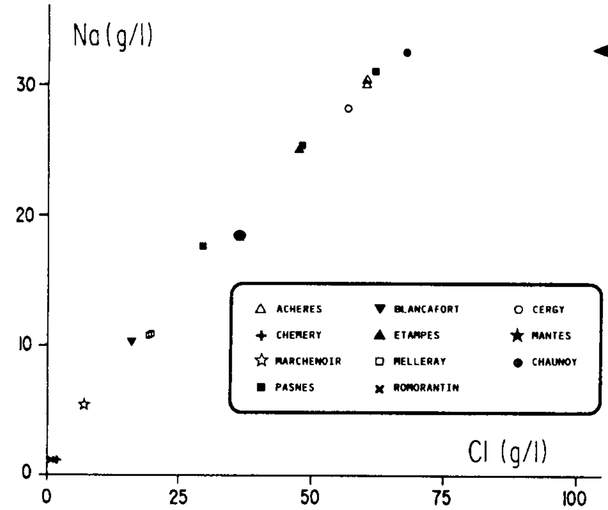


Fig. 2 - Plot of sodium versus chloride contents for the Triassic fluids.

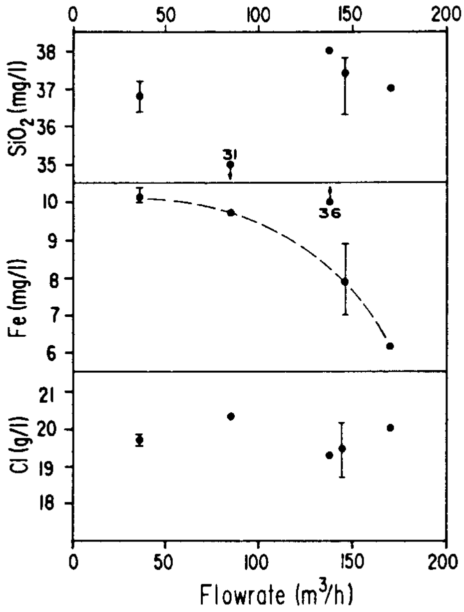
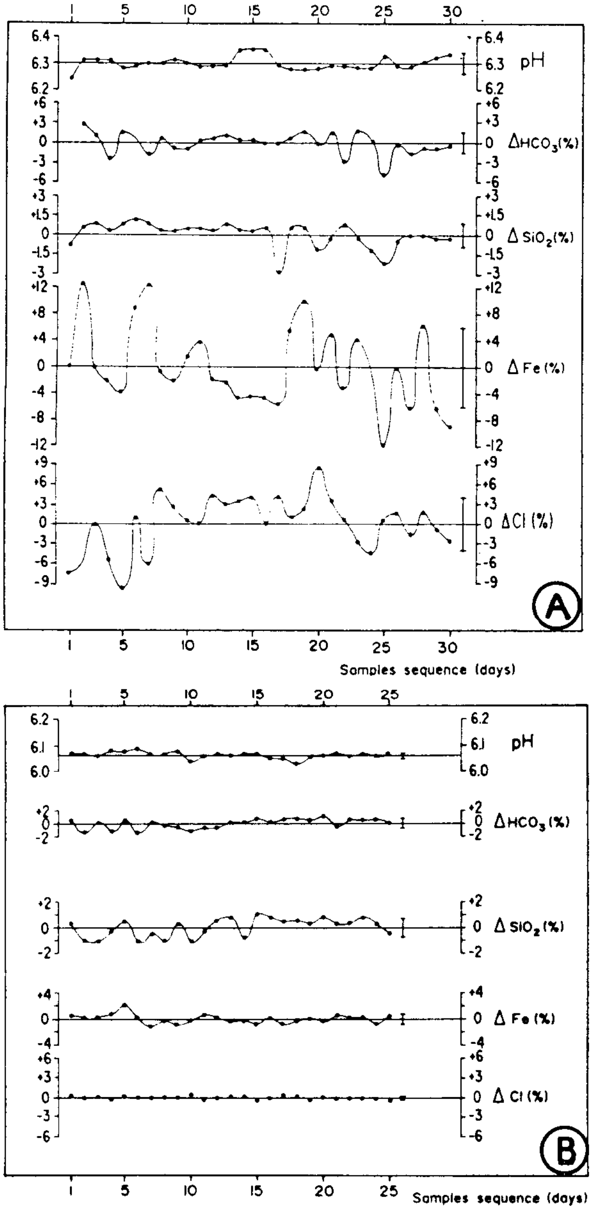


Fig. 4 - Variation of selected dissolved species in the geothermal fluid for various production rates of well GMY 1.

Fig. 3 - Time variations of pH and selected chemical species, expressed in % around the mean. Errors-bars correspond to 1 standard deviation.
A : 1st survey under pumping ($148 m^3/h$)
B : 2nd survey under artesian flow ($\sim 36\ m^3/h$)



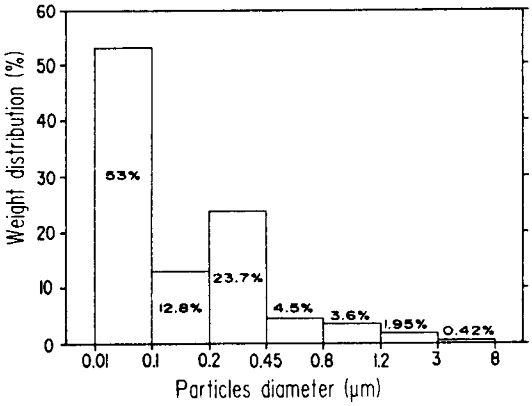


Fig. 5 - Distribution of particle sizes in the geothermal fluid at $36\ m^3/h$. Percentages are calculated from the particle load weighed on 8 filters.