

H₂S ABATEMENT IN THE COLD GAS CAP OF GEOTHERMAL WELLS BEFORE KICK-OFF TESTS

Culivicchi G., Lenzi A., Perini R., Tarquini B.

ERGA, ENEL Group- Larderello Laboratory UNIT, Piazza Leopolda 1 - 65044 (PI) ITALY

Key Words: geothermal, geochemical, H₂S abatement, environmental control, well, well performance tests

ABSTRACT

A new system for in-well H₂S abatement before kick-off tests has been developed. In this process, the H₂S present in the cold gas cap in the upper portion of the well is removed by treating the gas with a hydrogen peroxide solution at neutral pH. The reactant is continuously pumped with a special injection head descending along the well. Results of a field experiment are reported showing the reliability of the process. ENEL has adopted the reported technology and is currently using this method in the treatment of shallow cold gas cap before well kick-off tests whenever an atmospheric gas discharge is necessary for the well performance test.

1. INTRODUCTION

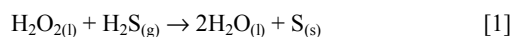
An important step in performing discharge tests of geothermal wells is removal of cold shallow gas cap from the well. The cold cap is formed during the cooling of the upper part of the well. At this level, a significant fraction of the Non Condensable Gases (NCG: mainly CO₂ and H₂S) is segregated from the condensed water and forms the so-called cold gas cap of the well. During the kick-off test the cold cap is usually discharged into the atmosphere and gradually replaced by the warm incoming steam. Although the total amount of CO₂ and H₂S discharged into the atmosphere is relatively low, in some cases the low temperatures reached by the gas in the isenthalpic expansion to atmosphere lead to the formation of heavy layer of CO₂/H₂S at the ground surface. This phenomenon can generate relatively high concentrations of the two gases and makes their dispersion into the atmosphere difficult because of the layering phenomena of the cold gas, which is heavier than air. The concentration of H₂S normally present in NCG in Italian geothermal fluids ranges between 1% and 5%. In this condition and if the CO₂ levels reach concentrations above the allowed working limits, the H₂S levels may exceed the threshold limit values currently accepted for this compound. This requires interruption of the test or reduction of the discharge flow rate (the gas discharge must be very fast in order to allow an internal gas lift effect on the water level and start of steam upflow). For instance, a 5000 ppmv peak ground concentration of CO₂ can result in H₂S concentrations ranging between 50 and 250 ppmv, requiring suspension of the kick-off. Smell problems may also require an abatement of H₂S, for instance, when the test is conducted near villages. ENEL has responded by adopting a preliminary H₂S abatement program as the initial step for all the well-performance tests. This paper discusses the results of our experiments and describes the methods adopted.

2. DESCRIPTION OF THE PROCESS

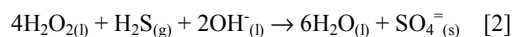
Several abatement processes for geothermal fluid treatment have been described, ranging from alkaline H₂S adsorption and H₂O₂ oxidation, as referred by Turner and Rex (1978), to Iron chelates catalysed processes, described by Hirtz and

Phee (1989) and by Bedell and Hammond (1988). In some cases the H₂S oxidation is covered by US Patent royalties (see references), and is chiefly used for H₂S removal in the NCG discharged into the atmosphere (primary H₂S emissions). It may also be combined with conventional processes developed for the oil and gas industry (e.g. Stretford, LO-CAT, Sulferox and others) for primary-secondary emissions control, where secondary emission originates from H₂S stripping in the cooling towers.

We have performed direct in-well treatment by injection of oxygen peroxide (H₂O₂) solutions along the upper portion of the well from ground level to depths where temperature and pressure conditions could assure the reliability of the process. Reaction with oxygen peroxide (H₂O₂) at neutral pH follows the scheme:



while the alkaline reaction has the following stoichiometry:



We have used neutral pH H₂O₂ solutions reaching only a partial oxidation of H₂S to sulphur [1]. This has allowed us to avoid a second NaOH line in order to perform an alkaline reaction. Moreover, a single pipe for NaOH/H₂O₂ solutions was unacceptable due to the instantaneous decomposition of H₂O₂ solution in alkali media.

The process involves a biphasic reaction between liquid H₂O₂ solution and gaseous H₂S and special precautions have been taken to assure the best mixing condition of the reagents. For this reason, the abatement was performed with an apparatus allowing a continuous flow of H₂O₂ solution and a constant and continuous descent speed of the injection head along the well (Fig. 1). This apparatus has allowed us to control contact times between gas phase and reaction solution by adjusting the speed of the injection head and flow rate of the reaction solution. Special care has also been taken in choosing the hydrogen peroxide storage materials and for the pump and injection line owing to the extreme decomposition susceptibility of hydrogen peroxide.

3. MATERIALS AND EXPERIMENTAL APPARATUS

The treatment was performed using a 20% (p/v) H₂O₂ solution. This concentration was a good compromise between low volumes utilisation and security restrictions. In fact, special care must only be taken with H₂O₂ concentrations above 36% by weight, as Meidl (1970) reports.

The H₂O₂ undergoes spontaneous decomposition in contact with several kinds of materials. In particular, organic materials or certain alloys can catalyse the reaction. For this reason, the entire injection line, including pump chamber, pipelines and injection head, is made of AISI 316 stainless steel to avoid spontaneous decomposition of the reagent. Moreover, the entire reinjection line was previously treated by fluxing a 10% NaOH solution for about 2 hours. After treatment, the line was rinsed with flowing water and then the abatement began.

The solution was injected with the equipment described in

Fig. 1. The volumetric pumps P_1 transported the H_2O_2 solution stored in tank S_1 while the P_2 pump was used as a supply. The coiled tubing in V_{10} and the injection head were introduced in a well through a stuffing box and allowed to descend in the well at a constant speed of about 2 m/s. The head of the tube was engaged to a centralizer. Finally, the solution was sprayed through injection nozzles.

4. MEASUREMENTS AND ANALYTICAL METHODS

Although this paper specifically refers to treatment performed on the FRANATE 2A well, the procedure can be generalised. The temperature and pressure in the well were measured with a mechanic probe (KUSTER type) positioned down to 600 m depth (Table 1). The pressure measurement allowed for the calculation of the maximum depth compatible with pump features and the pressure drop in the line. The temperature measurements indicated the maximum depth reachable with sufficient oxygen peroxide stability.

The gas in the well was sampled (2 sub-samples) at different depths and introduced in 300 ml volume glass sampling vials using the injection line as the gas carrier. The injection/sampling head was positioned at the proper depth, the gas, fluxed as far as the top of the line, was reached and then sampled. The gas sampling was repeated 24 and 72 hours after treatment to check H_2S recovery in the well. The H_2S and the main gas component concentrations were measured with the chromatographic method using a gas chromatographer equipped with a molecular sieve column for $H_2/CH_4/N_2/O_2$ determination and a silica filled packed +column for CO_2 and H_2S determination. The carrier gas was He. The Gas chromatographer had a thermoconductibility detector (TCD) with a detection capacity in the range of 100-20000 ppmv. The detection mode, gas flow rates and working temperatures for gas chromatographic determination were chosen according to an internal analytical protocol used at the Larderello Laboratory Unit.

5. RESULTS OF GAS TREATMENT

The treatment was performed between ground level and a 400 m depth. The temperature and pressure indicate that between 300 and 400m depth the cold cap gas is completely replaced by saturated vapour. A slight discrepancy between calculated vapour saturated pressure and observed total pressure was, however, observed due to difficulties encountered during temperature/pressure measurements. This in turn suggests that a 400m depth could be considered a practical maximum reachable depth (Fig 2).

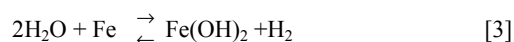
The data in Table 1 and the gas composition given in Table 2 have been used to determine the amount of H_2S present in the well. It is calculated by correcting the total measured pressure in the well for steam saturation pressure at the corresponding temperature. The stoichiometric amount of H_2O_2 needed for reaction was then calculated giving the following treatment parameters:

1. H_2S in the well : ~ 8 kg
2. Stoichiometric H_2O_2 : ~40 kg
3. 10 times excess H_2O_2 : 400 l
4. discharge time 5 h at $q=80$ l/h
5. double treatment by descending and ascending the 400 m, corresponding to a 800 m travel with an average speed of 2/3 m/min

Table 3 shows that treatment has almost completely removed H_2S from the well, at least below the detection limit of the analytical technique (100 ppmv) corresponding to an average

99% abatement yield. The low H_2S concentrations persisted after 72 h, indicating that the method could prevent gas mixing and that no H_2S recovery occurred from the bottom of the well during treatment. Although we did not observe appreciable H_2S recovery due to gas mixing, in general, the latter phenomenon cannot be completely prevented. This depends on the peculiar characteristics of each well.

The gas analysis indicates that, except for H_2 and O_2 , there is no appreciable variation in the composition of the gas in the well. The O_2 concentration increase can be explained by a partial decomposition of the H_2O_2 solution. The H_2 increase is determined by a variation in the oxidation properties of the fluid that has changed from a strongly reducing environment in presence of H_2S to a more oxidizing environment in presence of O_2 and moisture. These conditions may have favored the oxidation of the iron contained in the well-casing according the following reaction:



with formation of Hydrogen.

The H_2S abatement equipment is shown in figure 3.

The amounts of flammable compounds, mainly H_2 and CH_4 , are compatible with flammability limits normally reported in literature, see Meidl (1970) and Pasquon.

REFERENCES

- Turner T. A., Rex R.W. A practical hydrogen sulfide abatement process for air drilling and venting geothermal steam wells. *GRC Trans.* Vol. 2 (1978).
- Hirtz P., Phee T. M. Development of a Safer and More Efficient Method for Abatement of H_2S during Geothermal Well Drilling. *GRC Trans.* Vol. 13 (1989)
- Bedell S. A., Hammond C. A. H_2S Abatement During Air Drilling of Geothermal Wells. *GRC Bull.* (1988)
- U.S. Patent Number 5096691 (Mar. 17 1992). *H₂S abatement with stabilized chelates in geothermal drilling.*
- Meidl, J. H. (1970). *Flammable hazardous materials.* Collier Macmillan Publisher, Glenco Press.
- Pasquon, I. *Rischi potenziali. Sicurezza e protezione ambientale nell'industria chimica.* Ed. CLUP Milano.

Table 1: Temperatures and pressures measured in the well

Depth (m)	Temperature (°C)	Pressure (bar)
0	24.1	21.0
100	24.1	20.9
200	67.7	20.9
300	103.5	20.7
400	221.9	20.5
500	223.4	20.4
600	223.9	20.3

Table 2: Calculated Hydrogen sulphide in the well

Depth (m)	V (m ³)	Press. (bar)	P-P _{vad} (bar)	NCG (moles)	H ₂ S (kg)	H ₂ S (%V)
		21	20.97			0.85
0 – 100	9.06	20.9	20.87	7881	2.1	0.68
100 – 200	9.06	20.9	20.62	7281	1.6	0.63
200 – 300	9.06	20.7	19.55	6270	2.4	1.59
300 – 400	9.06	20.5	~0	2512	1.9	2.75
400 – 500	9.06	20.4	~0	~0	~0	1.07
500 – 600	9.06	20.3	~0	~0	~0	
				Tot	7.9	

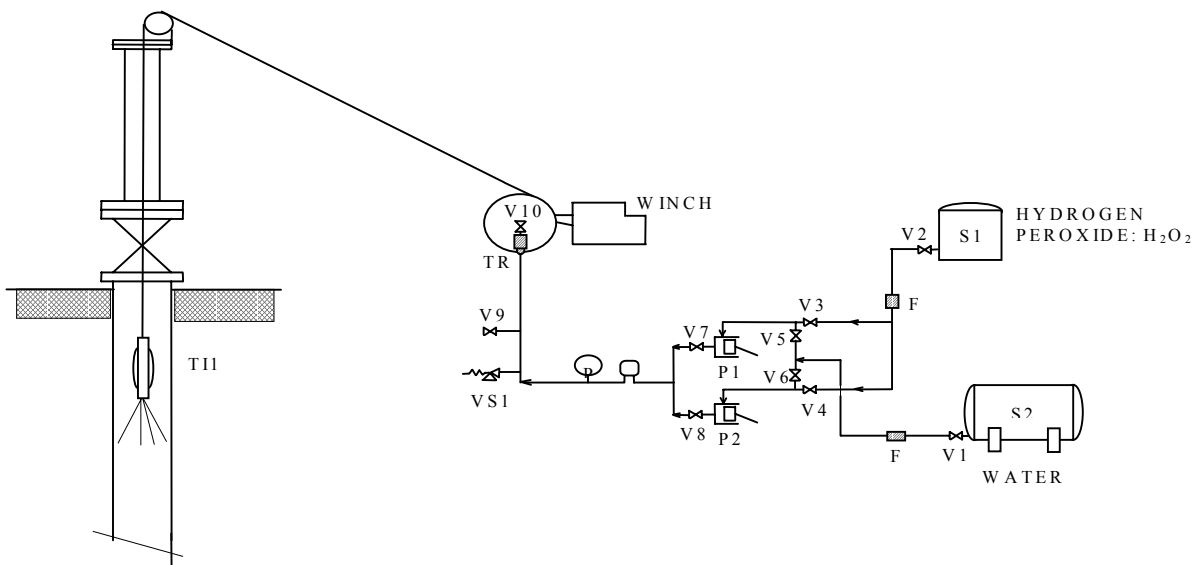


Fig. 1: Scheme of the pumping device used in the in-well H₂S abatement

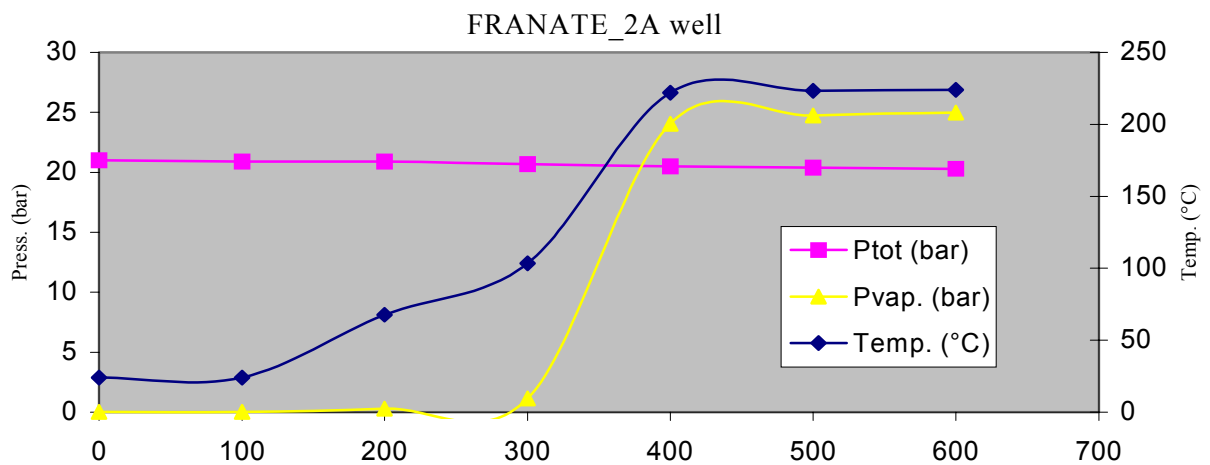


Fig.2: temperatures and pressures in the FRANATE_2A well

Table 3: Gas composition in the well before and after treatment as a function of depth

Gas composition before treatment						
Depth (m)	H ₂ (%V)	O ₂ +Ar (%V)	N ₂ (%V)	CH ₄ (%V)	CO ₂ (%V)	H ₂ S (%V)
0	4.18	0.01	0.48	0.75	93.73	0.85
5	4.78	0.01	0.52	0.73	93.28	0.68
100	5.71	0.01	0.74	0.77	92.15	0.63
200	8.63	0.01	0.53	0.70	88.54	1.59
300	12.52	0.02	0.67	0.68	83.34	2.75
400	7.19	0.10	0.81	0.72	90.10	1.07
Gas composition after treatment (24h)						
Depth (m)	H ₂ (%V)	O ₂ +Ar (%V)	N ₂ (%V)	CH ₄ (%V)	CO ₂ (%V)	H ₂ S (%V)
0	8.50	0.74	0.68	0.69	89.08	<0.01
50	12.80	1.80	0.52	0.62	84.30	<0.01
100	18.00	0.26	0.43	0.53	80.80	<0.01
200	7.92	1.66	0.55	0.66	89.19	<0.01
400	7.85	2.36	0.53	0.66	85.57	<0.01
Gas composition after treatment (72h)						
Depth (m)	H ₂ (%V)	O ₂ +Ar (%V)	N ₂ (%V)	CH ₄ (%V)	CO ₂ (%V)	H ₂ S (%V)
0	8.56	0.01	0.68	0.67	88.59	<0.01
50	8.21	0.93	0.51	0.66	89.67	<0.01
100	12.96	1.83	0.48	0.64	84.08	<0.01
200	17.96	0.01	0.47	0.55	81	<0.01



Fig. 3: Injection line and pump station