GEOTHERMAL GASES AS A SOURCE OF COMMERCIAL CO₂, IN MIRAVALLES, COSTA RICA AND HAEDARENDI, ICELAND

Rodolfo Bogarín Chaves
Instituto Costarricense de Electricidad,
Departamento de Recursos Geotérmicos,
Campo Geotérmico Miravalles, Guayabo, Guanacaste
COSTA RICA

ABSTRACT

The production of commercial liquid carbon dioxide (CO_2) is an option for the utilization of the byproducts of geothermal power plants. Recovery of CO_2 from non-condensable gases from geothermal fluids is the subject of this paper. A general description of the non-condensable gases found in different geothermal fields and their dependance on reservoir temperature is presented. The composition, quantities and the flow of non-condensable gases in the Miravalles Geothermal Field in Costa Rica is described. Case histories from Haedarendi, Iceland and Kizildere, Turkey geothermal fields are given as examples of actual CO_2 production. Finally, the production process is analysed in two parts: the removal of H_2S from the non-condensable gases and the CO_2 recovery by liquefaction.

1. INTRODUCTION

Geothermal energy has been widely used for heat and power generation. When used for electricity generation, it has several advantages over other energy sources, such as fossil fuel, due to less environmental impact. The principal environmental effects of geothermal energy are gas emanations and disposal of the waste water.

In the Miravalles geothermal field, Costa Rica, the brine is reinjected back into the reservoir but the gas emanations are discharged to the atmosphere. These gas emanations are not a major environmental problem, but the utilization of these gases for other industrial processes can improve the use of the resource as well as the environmental conditions in the area.

The production of CO_2 is one way to use the geothermal fluid as chemical feedstock. This process recovers the gas and produces liquid CO_2, which has many uses, for example in the food industry. This requires the purification of the CO_2. The H_2S is removed and can be transformed into elemental sulfur or harmless sulfur compounds with potential marketing in industries like the production of fertilizers.

Liquid CO_2 production from geothermal gas is found today both in Iceland and Turkey. The Haedarendi geothermal field in Iceland produces 550 tons per year, and the Kizildere geothermal field in Turkey, with a power plant of 20 MW, can produce 30,000 tons per year.

2. SOURCES OF GASES IN GEOTHERMAL FLUIDS

Geothermal reservoirs are a natural source of energy, for example for space heating or electricity production. At the same time, they are also a source of non-condensable gases and mineral-rich water. In the production of electricity, the steam obtained from the geothermal reservoir is used to rotate the steam turbines to generate electricity. After going through the turbine, the steam is condensed (condensing turbines) or escapes to the atmosphere (back pressure turbines). In both cases, the non-condensable gases are released to the atmosphere.

2.1 Non-condensable gases in geothermal fields

The principal geothermal non-condensable gases are: CO_2, H_2S, N_2, CH_4, O_2, H_2, Ar, He and others in trace quantities. The major problem with such emanations is potential damage to the environment. Two specific cases are CO_2 and H_2S, the first due to its contribution to the global greenhouse effect, and the second because of its toxicity and for possibly being involved in the proliferation of acid-rain. The elimination of H_2S is an obligation in the United States, but most countries overcome the limits by ensuring proper dispersion into the atmosphere. In spite of the CO_2 and H_2S emanations, geothermal energy is more environmental friendly than traditional fossil fuel sources. In Figures 1 and 2, the emanations of CO_2 and H_2S are shown for different types of power plants. For both, emanations from geothermal plants (Krafla, Iceland and Miravalles, Costa Rica) are lower than the emanations from fossil fuel plants (Ármannsson and Kristmannsdóttir, 1992). The data for Figures 1 and 2 are shown in Appendix 1.
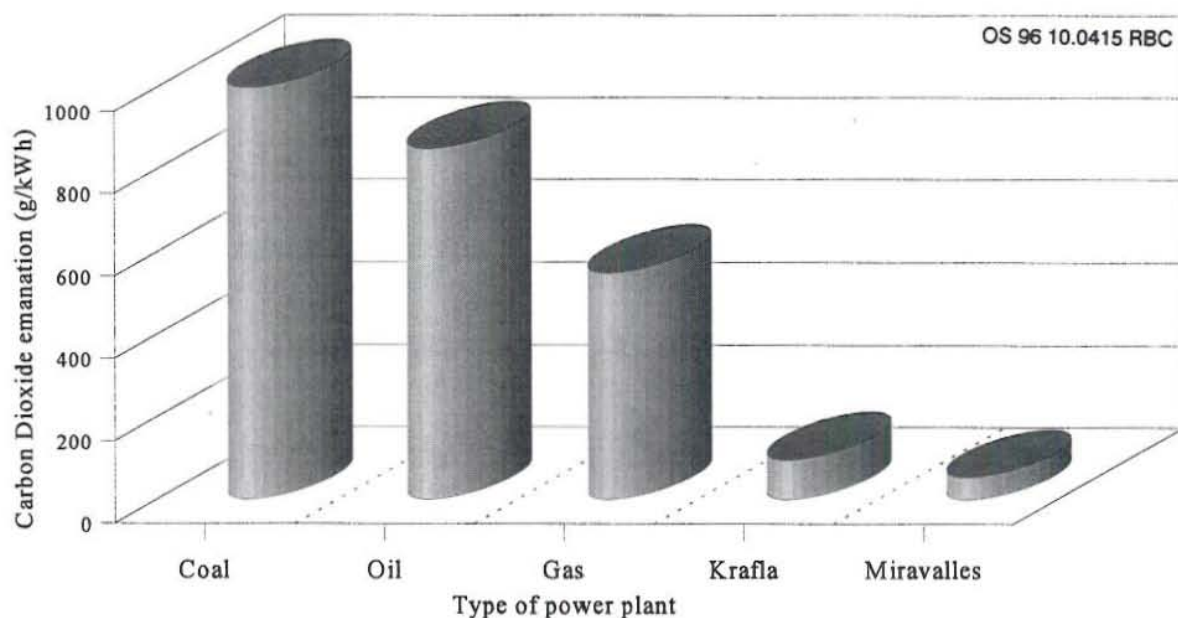

FIGURE 1: Emanations of CO_2 for different types of power plants showing the Krafla and the Miravalles geothermal power plants (Modified from Ármannsson and Kristmannsdóttir, 1992)
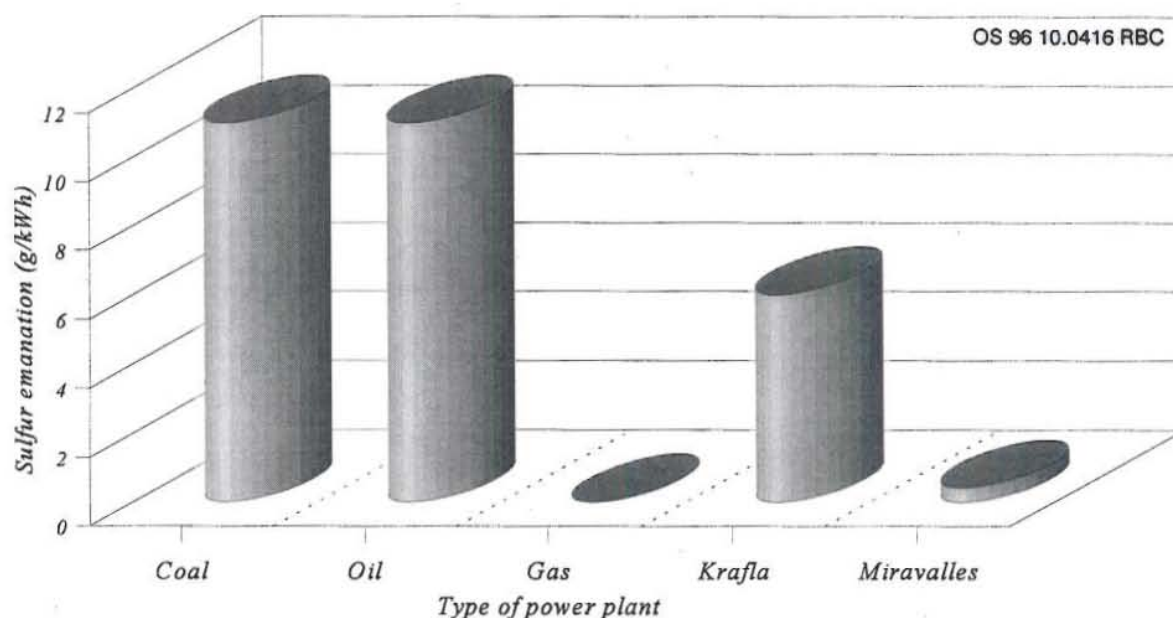
OS 96 10.0416 RBC

FIGURE 2: Emanations of H_2S, reported as sulfur, for different types of power plants; the Krafla and Miravalles geothermal power plants are shown as examples for geothermal plants (modified from Ármannsson and Kristmannsdóttir, 1992)

The composition of the non-condensable gases in the steam is characteristic of each reservoir. The composition from eight geothermal fields is shown in Figure 3. It is clear that the content of each gas is somewhat different for each reservoir but the CO_2 fraction of the gas is relatively constant and close to 90% by weight for high-temperature fields. Data for the eight geothermal fields is reported in Appendix 2.

OS 96 10.0276 RBC

Olkaria (KEN)   Wairakei (NZ)   Ngawha (NZ)   Zunil (GUAT)
Miravalles (CR)   Svartsengi (IS)   Hveragerdi (IS) Krafla (IS)
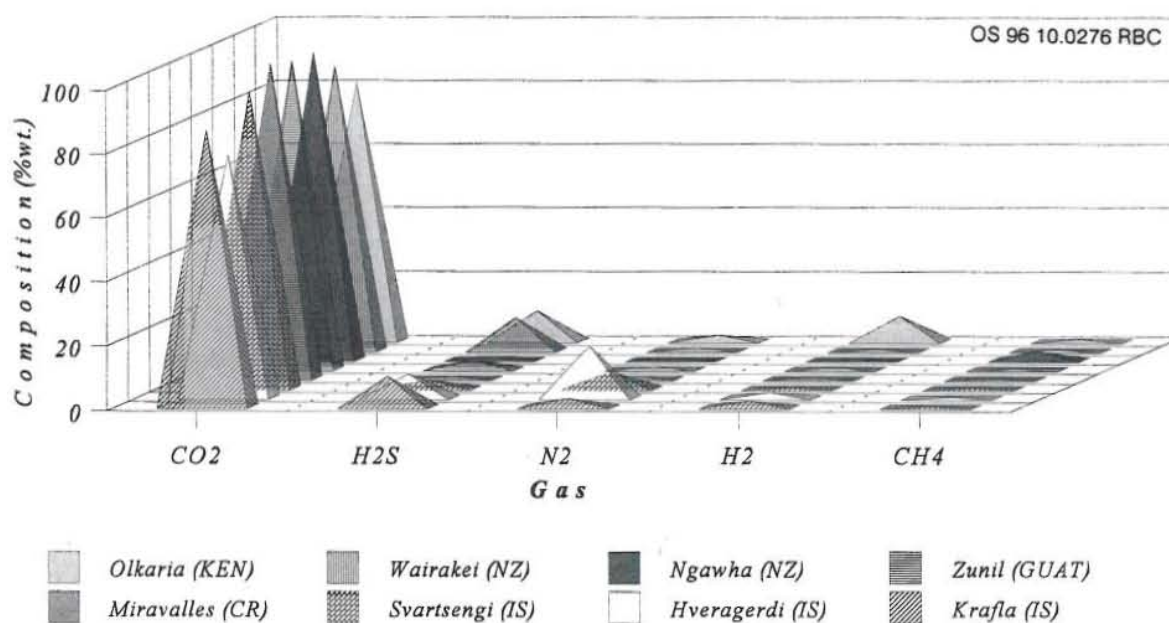
FIGURE 3: Composition of non-condensable gases from eight different fields

2.2 Utilization of the non-condensable gases in geothermal activities

The non-condensable gases are widely used in geothermal exploration and exploitation as indicators of the reservoir conditions, especially of the temperature. Gas geothermometers have been developed by geochemists to give estimations of the reservoir temperature from the type and concentration of gas and ratios between the concentrations of individual gases.

In the preliminary exploration phase for geothermal resources, these gases are very useful. Surface manifestations, like steam vents and fumaroles, give the first information about temperature and minerals in the reservoir from studies of the gas equilibria. The gases sampled from the borehole fluids are also used in the estimation of the temperatures in the reservoir, for reservoir monitoring, and to optimize the utilization of the geothermal resource.

Normally the gases used for geothermometry are: CO_2, H_2S, N_2, H_2, CH_4, Ar and He. These can be divided into two groups. The gases in the first group are called "tracers", and are noble gases like Ar and He or relatively inert ones like N_2. The second group of gases interacts with the rock; examples of these are CO_2, H_2S, H_2 and CH_4 (Giggenbach, 1991).

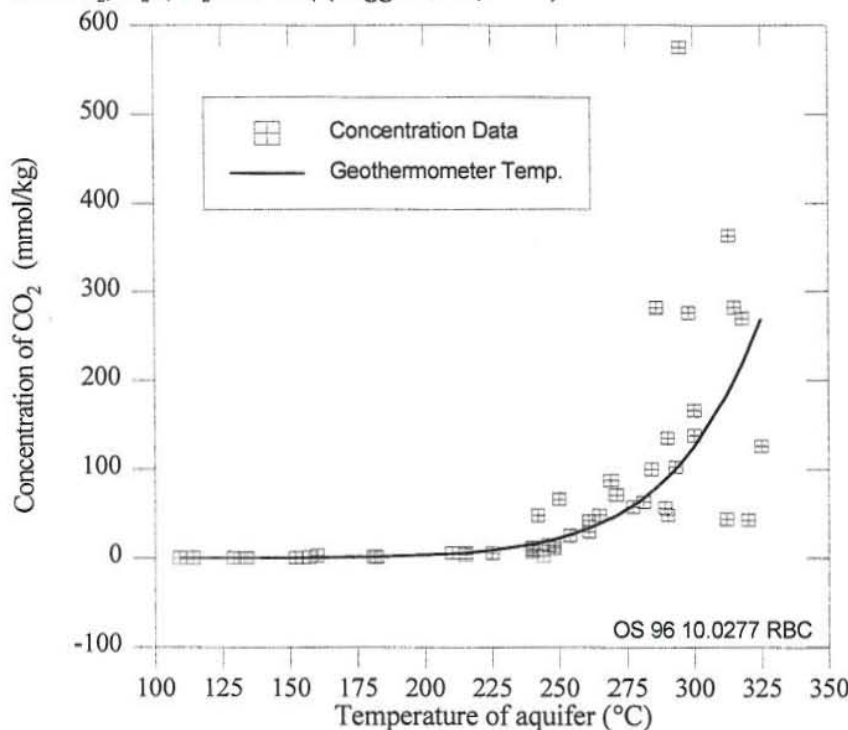
FIGURE 4: Concentration of CO_2 and temperature of the aquifer used for the calibration of the geothermometer (modified from Arnórsson and Gunnlaugsson, 1985)

The basis for the utilization of the concentration of these gases as geothermometers, is the establishment of equilibria between the rock and the gas at the temperature and pressure of the reservoir. By the utilization of these equilibria, it is possible to define a correlation between the temperature in the reservoir and the concentration of the gases in the sample. Arnórsson and Gunnlaugsson (1985) calibrated gas geothermometers with data from many fields around the world. The good correlation between the temperature and the concentration of the gases is clear. This correlation for CO_2, H_2S and H_2 is shown in Figures 4, 5 and 6. The data points are the temperature measured in the aquifer and the lines are the fits to Equations 1, 2, 3, 4 and 5 proposed by Arnórsson and Gunnlaugsson (1985) as geothermometers for each gas. In the case of CO_2, the correlation is good for all the temperatures, and the following equation holds (see Figure 4):

$$\log(conc.CO_2) = -1.09 - \frac{3894.55}{T} + 2.532 \log T \qquad (1)$$
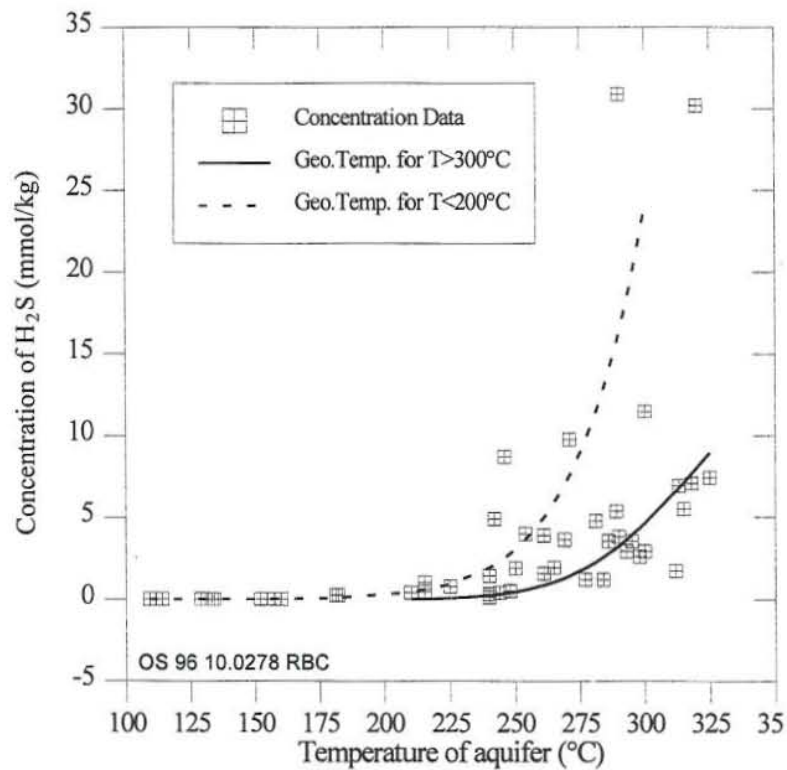
where   T   = Reservoir temperature (°K).

FIGURE 5:   Concentration of H₂S and temperature of the
aquifer used for the calibration of the geothermometer
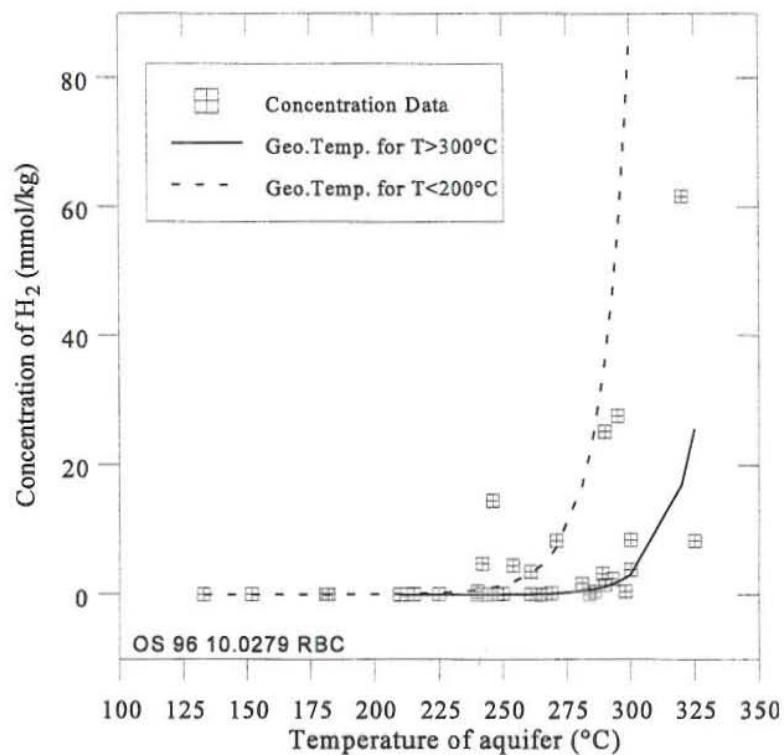(modified from Arnórsson and Gunnlaugsson, 1985)

FIGURE 6:   Concentration of H₂ and temperature of the
aquifer used for the calibration of the geothermometer
(modified from Arnórsson and Gunnlaugsson, 1985)

For temperature dependence of H_2S and H_2, two different sets of equations for two different sets of temperatures and salinities are defined. The first set describes the dependence between the temperature and the concentration of H_2S and H_2 at temperatures above 300°C and at temperatures between 200 and 300°C if Cl > 500 ppm. These equations are (see Figures 5 and 6)

$$\log(conc.H_2S) = -11.80 - 0.06035\,T - \frac{17691.09}{T} + 27.163\,\log T \tag{2}$$

and

$$\log(conc.H_2) = -3.04 - \frac{10763.54}{T} + 7.003\,\log T \tag{3}$$

The second set describes the temperature dependence of H_2S and H_2 at temperatures below 200°C and between 200 and 300°C if Cl < 500 ppm. These equations are (see Figures 5 and 6)

$$\log(conc.H_2S) = -1.24 - \frac{4691.84}{T} + 2.830\,\log T \tag{4}$$

and

$$\log(conc.H_2) = 11.98 + 0.08489\,T + \frac{8254.09}{T} - 27.587\,\log T \tag{5}$$
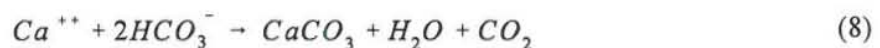
2.3 CO_2 in geothermal fields

CO_2 is the major component of non-condensable geothermal gases. In high-temperature fields it is typically close to 90% by weight of the gases. The origin of this gas in the reservoirs has been explained in different ways. The primary source is usually organic or magmatic. Four of the most common mechanisms for the formation of CO_2 gas in the reservoir are described by Michels (1979). The first is a simple phase change due to change in pressure conditions when the fluid emerges at the surface

$$CO_{2(g)} \rightleftharpoons CO_{2(l)} \tag{6}$$

The second one is the dissociation of bicarbonate, according to the equation

$$2HCO_3^- \rightarrow H_2O + CO_3^- + CO_2 \tag{7}$$
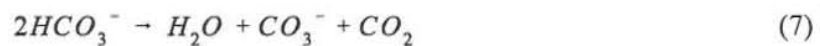
The third is the result of calcite precipitation

$$Ca^{++} + 2HCO_3^- \rightarrow CaCO_3 + H_2O + CO_2 \tag{8}$$

And the fourth one is associated with proton consumption and described by

$$H^+ + HCO_3^- \rightarrow H_2O + CO_2 \tag{9}$$

The relative effect of these processes is different in different geothermal fields, due to the different characteristics of the reservoirs. For example in East Mesa, USA approximately 80% are formed in the first process, 20% in the second and 2% for the third and fourth combined (Michels, 1979).

3. MIRAVALLES GEOTHERMAL FIELD

3.1 Flow diagram of non-condensable gases

Figure 7 describes the flow of non-condensable gases from the production wells through the 60 MW electricity power plant at Miravalles, and finally to the atmosphere.
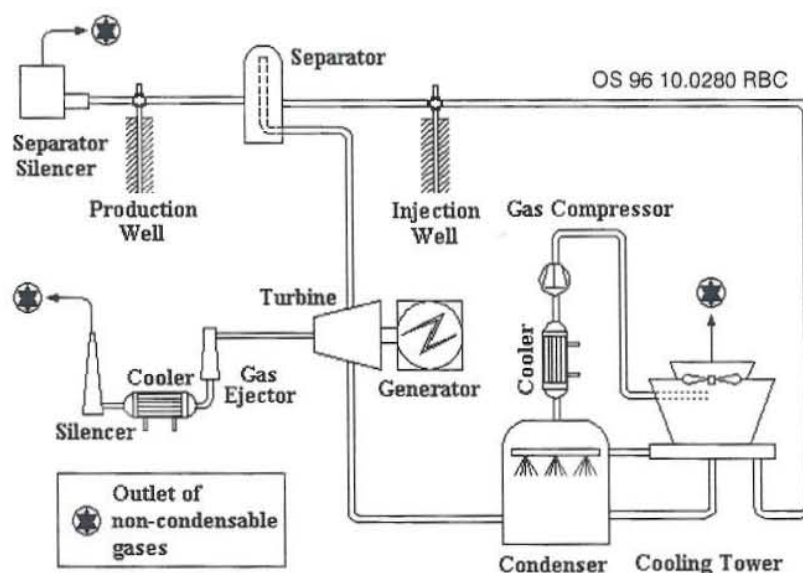
FIGURE 7: Present points of outlet for non-condensable gases
in the 60 MW Miravalles power plant

The non-condensable gases emanate from the reservoir with the biphasic fluid from the production wells. The flow from the wells can be delivered directly to the atmosphere through the separator-silencer if the wells are out of production. In normal operation the flow is sent to the centrifugal separators from which the steam and gas goes to the turbine. The separated brine is reinjected.

The steam rotates the turbine, and in combination with the generator, produces electricity. At this point the gas ejector system can extract the non-condensable gases from the turbine condenser. This gas is cooled down and is released to the atmosphere via the cooling tower for dilution and good dispersion in the atmosphere.

3.2 Composition and quantities of non-condensable gases

In the Miravalles geothermal field, the non-condensable gases are: CO_2, H_2S, N_2, CH_4, O_2 and H_2. The composition of the gas steam released from the power plant is reported in weight percentage, the concentrations in mmol/kg of steam and the flow of gas in tons per year, as shown in Table 1.

TABLE 1: Composition, concentrations and flows of non-condensable gases
from the 60 MW plant in the Miravalles geothermal field

Type of gas	Weight percentage	Quantities of gas in the steam (mmol / kg of steam)	Flow of gas (tons / year)
CO_2	96.43	138.0	28 695.2
H_2S	1.01	1.45	232.5
N_2	2.49	3.57	471.4
CH_4	0.01	0.01	0.8
O_2	0.13	0.18	27.2
H_2	0.02	0.03	0.3

The present (1996) total production from Miravalles is approximately 916 kg/s of biphasic fluid, the steam produced is 149 kg/s and the liquid 767 kg/s.

4. GAS TREATMENT

4.1 CO_2 recovery process

Carbon dioxide is a gas widely used, for example in soft drink production, dry ice production, and for recharging fire extinguishers. Common sources of CO_2 are: combustion gases, chemical reactions, brewery fermentation and, in at least two cases, geothermal gases. Independent of the source, the CO_2 must be purified, the grade of purity coincides with the final application (greenhouses, conservation of foods, soft drinks, etc.). The CO_2 plant can be divided into the following different sections: cleaning the gas (specifically of H_2S), compression-cooling, drying, final cleaning, condensation and storage (Quintero, 1987). In Figure 8 the flow diagram for liquid CO_2 production is shown, and the different sections of the process indicated (Union Construction; Buse Anlagenbau).

4.1.1 Cleaning of gases, removal of H_2S

The gas streams used for the production of CO_2, especially from geothermal sources, contain H_2S. This gas must be eliminated. The principal reasons are high toxicity and commercial considerations (odour). Many different processes are available for the abatement of H_2S. The main cleaning processes will be discussed in section 5.2.

4.1.2 Compression of CO_2

The compression process is normally carried out in two or more stages. Figure 9 shows the compression equipment for two stages. Each stage is composed of a piston compressor, a cooler and a condensate trap. The compressor normally increases the pressure of the gas in the first stage from 0 to 5-7 bar-g and

in the second from 5-7 to 15 bar-g. Also, the temperature increases due to the adiabatic compression. For this reason, the cooler is the next step in order to decrease the temperature in each step and to keep it close to 30°C. The condensate trap is required for the evacuation of liquid generated due to compression and cooling processes and for the reduction of moisture before the drying process.
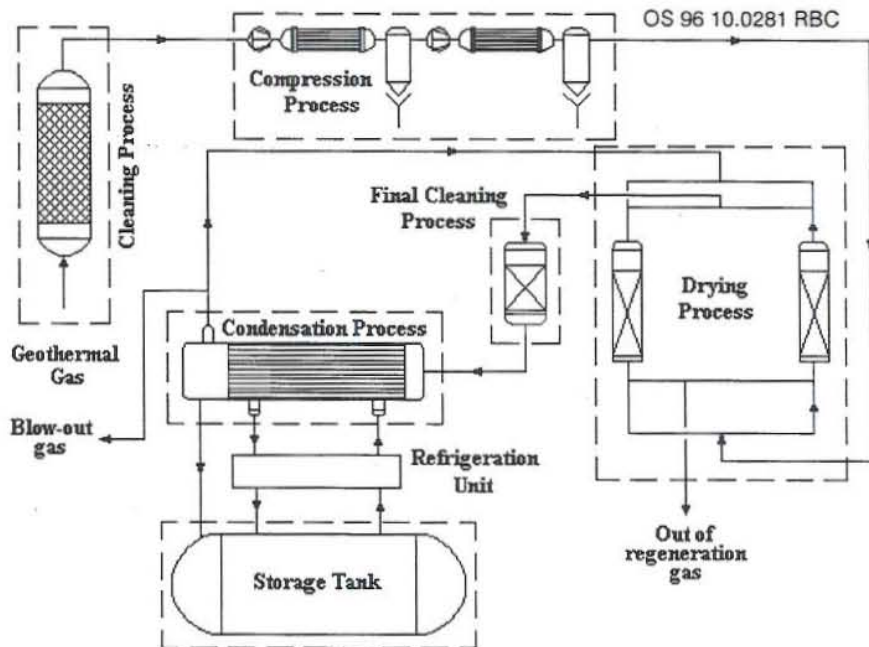

FIGURE 8: Flow diagram for the CO_2 production process

4.1.3 Drying process

The drying of the gas is carried out with two packed columns with a molecular sieve dehydrator. The gas is dried to a dew point of approximately -60°C. The reason for the use of two columns is the regeneration of the dehydrator; the drying process takes place in one column while the other column is being regenerated.

The gas from the compression process goes through one column and the dehydrator absorbs the moisture. Then, the gas is sent to the final filtration process. The dehydrator in the column will become saturated and then the gas flow is shifted to the other column. At this time the regeneration of the dehydrator begins with dry gas from the condenser (CO_2 and blowout gas) in a counter flow stream. Figure 10 explains the drying process.
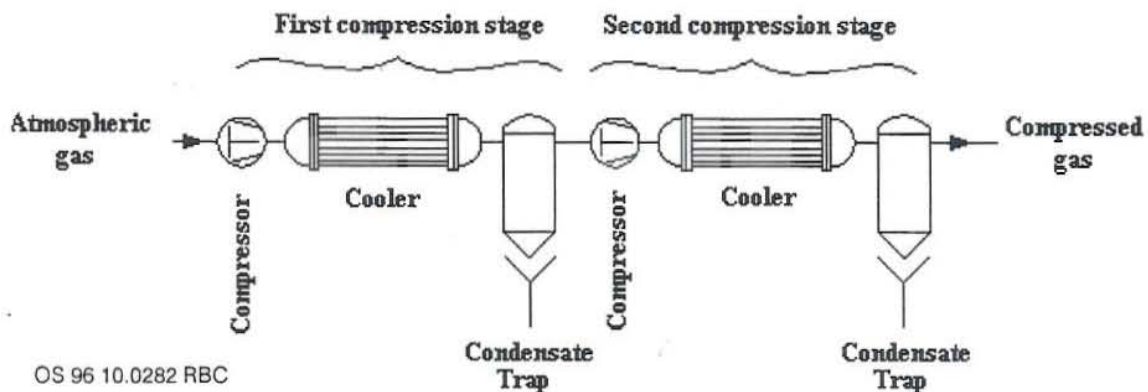

FIGURE 9: Scheme of the compression process for the CO_2 gas

4.1.4 Final cleaning process

The final cleaning process is for the elimination of impurities and odour, normally from traces of H_2S, oil from the compressors, etc. For H_2S, the first cleaning process removes close to 99%, which is usually satisfactory for environmental requirements. For production of food grade CO_2, an additional polishing process is required.

The most common processes for final cleaning are: Potassium permanganate scrubbing and activated carbon filtration. In the first case the gas is scrubbed in a tower with dilute solutions of $KMnO_4$ and in the second one the gas is filtered in a packed tower with activated carbon. The reposition of the reactive in the scrubbing process and the activated carbon in the filtration process is required, but the cost of both processes is modest.
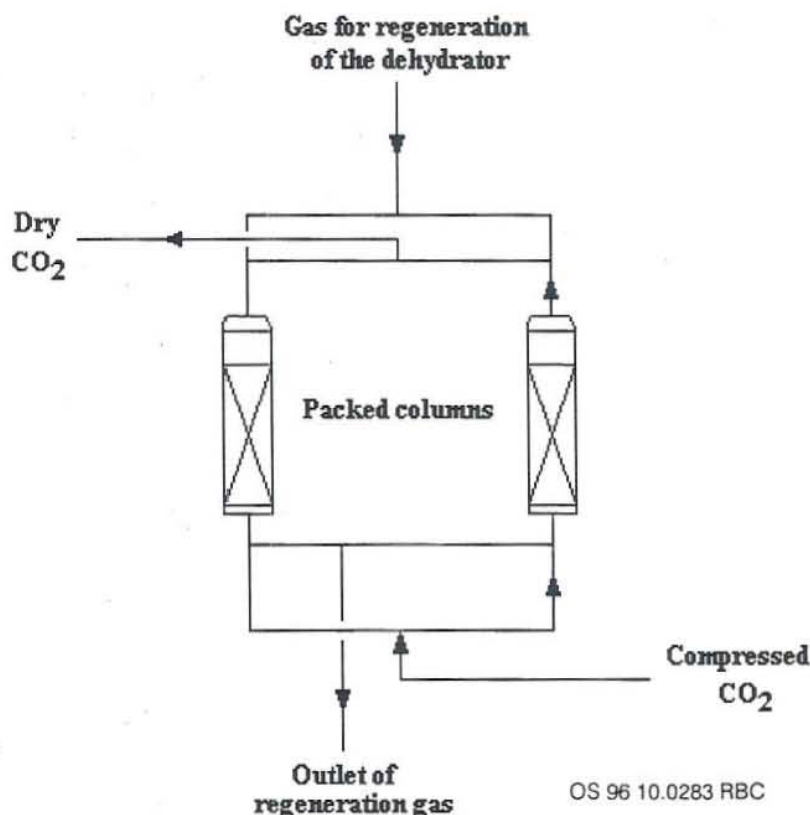

FIGURE 10:   Scheme of the drying process for CO_2 gas

4.1.5 Condensation process (liquefaction)

The aim of the condensation process is the change in the phase of CO_2 to liquid by a decrease in temperature (-30°C approximately) in combination with high pressure in the system. The gas from the final filtration process is condensed and the CO_2, in liquid phase, is sent to the storage tank. The non-condensable gases and a small fraction of CO_2 are split into two streams, one for blowout to the atmosphere, and the other is used for the regeneration of the dehydrator in the drying process. The cooling fluid comes from a refrigeration equipment. This equipment may cool the condenser only or the condenser and the storage tank. Sometimes the storage tank is cooled with CO_2 from the same process. Figure 11 shows schematically the condensation process.

4.1.6 Storage tank

The storage tank is designed to contain liquid CO_2 at a pressure of 15 bar-g and a temperature of -30°C. It is an insulated tank with a cooling system. The cooling system, in some cases uses the CO_2 from the process and, in some cases, an independent cooling device.

4.2 Cleaning non-condensable gases, eliminating H₂S

For commercial production of CO_2, the removal of H_2S presents a problem. There are many different processes in use in the geothermal industry for the elimination of H_2S. The most important ones will be described in this chapter.

4.2.1 General classification of the H₂S abatement process

Sanopoulos and Karabelas (1995) divided the abatement

FIGURE 11: Scheme of the condensation process of the CO_2 gas

processes into four methods. The classification is based on the location: upstream or downstream of the generation turbine, and on the type of flow: geothermal steam, gas from the ejectors or condensate. These groups are described in Table 2 and illustrated in the power plant diagram in Figure 12.

TABLE 2: Description of the methods for H_2S abatement process

Method	Location	Type of flow
Method A	Upstream	Geothermal steam
Method B	Downstream	Off-gas ejector
Method C	Downstream	Condensate water
Method D	Downstream	Combinations of flows

Method A eliminates H_2S from the geothermal steam. The upstream methods have the potential advantage of reducing corrosion in the generation equipment, and improving generation efficiency through elimination of non-condensable gases before the turbine, but also carry the problem of thermal energy loss in the elimination process. This type of cleaning method has not yet been applied to geothermal plants.

The downstream methods eliminate H_2S from non-condensable gases after the turbine and condensation of the steam. Method B extracts H_2S from the gas phase. Normally these are chemical methods and the final product is elemental sulfur or harmless sulfur compounds. Method C removes H_2S from the turbine condenser condensate. This is considered a secondary abatement system and is normally used in combination with other methods. Method D uses a combination of the B and C methods, like primary and secondary abatement processes.
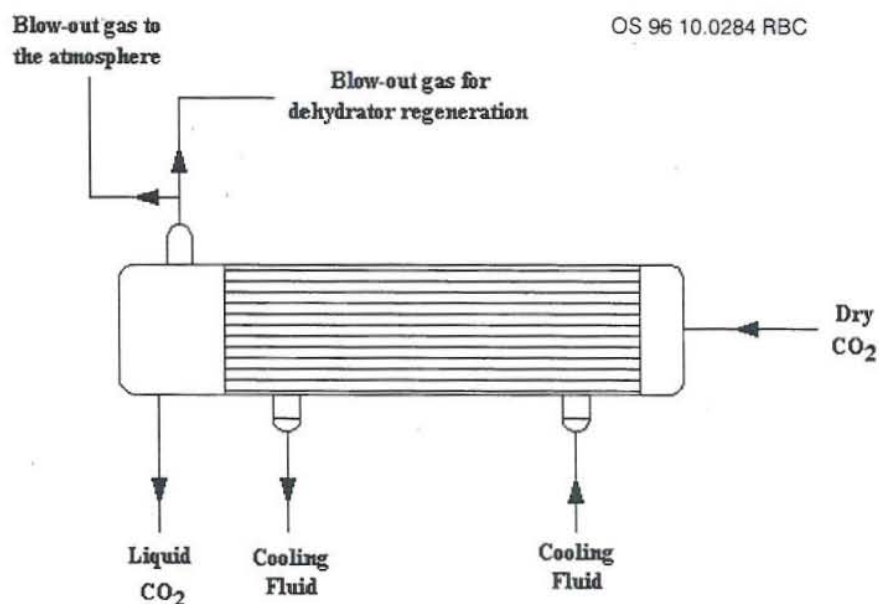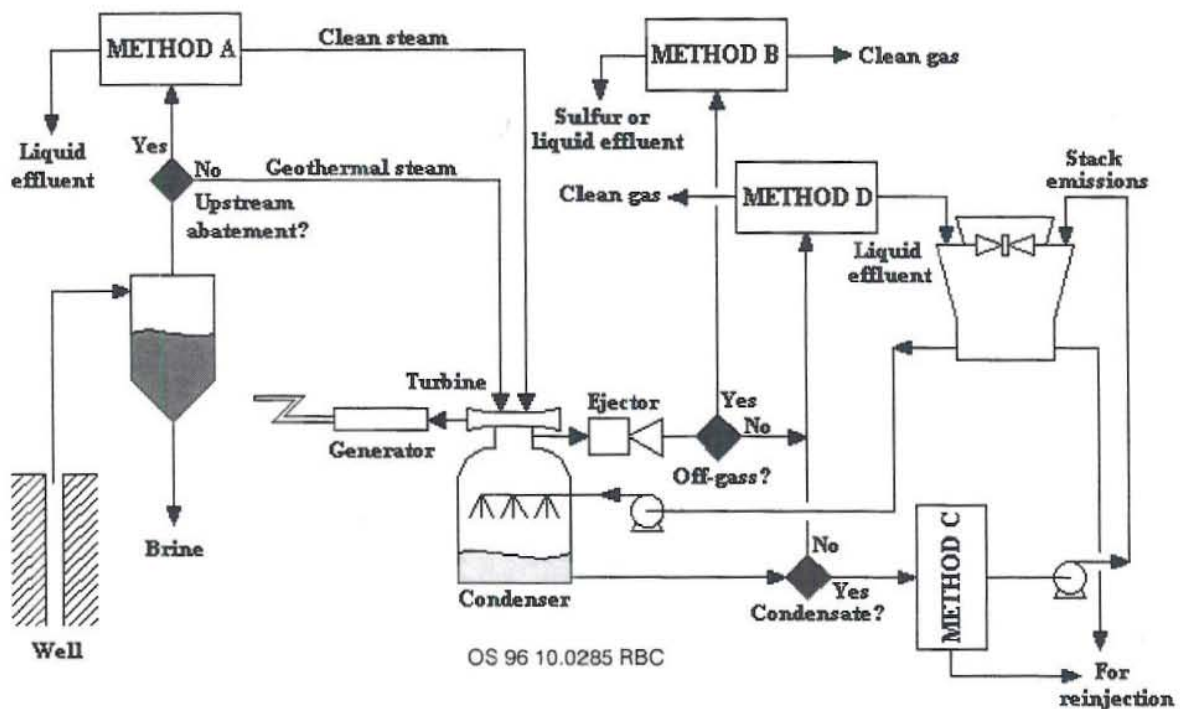
FIGURE 12: General classification of the H₂S abatement process
(modified from Sanopoulos and Karabelas, 1995)

4.2.2 Overview of some H₂S abatement processes

The H₂S abatement technology is known through the gas industry. Various processes have been proposed for the elimination of this gas. Ferguson (1975) and Sanopoulos and Karabelas (1995) describe the main processes for cleaning of H₂S and the production of elemental sulfur or harmless sulfur compounds.

Copper sulfate process
This process treats the H₂S in a scrubbing tower with an acid solution of copper sulfate in which the H₂S is transformed to copper sulfide. The pH is controlled with the addition of salts like ammonium sulfate. The copper sulfide precipitates and is recovered and transferred to the copper sulfate regeneration process. In the general classification of Sanopoulos and Karabelas, (1995) this is considered an upstream process.

Steam reboiler process
Elimination of H₂S using a steam reboiler is a primary process for the separation of H₂S gas from the main geothermal steam flow. The process is carried out by continuous condensation and reboiling of the geothermal steam. The non-condensable gases are separated with a small steam fraction. Then, the non-condensable gases are treated in a secondary process to reduce the amount of H₂S to the required concentration. Like the copper sulfate process, the steam reboiler is applied in the flow upstream of the turbine.

Alkali process
This process treats the gas by neutralization with alkali, generally with solutions of NaOH. The process is carried out in a scrubbing tower and can be used upstream or downstream of the turbine. The principal problem is high operation cost for consumption of chemicals.

Redox process

This process removes H_2S with reduction-oxidation chemical reactions; the most common reaction uses vanadium or iron as oxidation agents. This process is widely used. H_2S is transformed to sulfur or sulfur compounds. The main problem is disposal of waste sub-products, especially if they contain traces of vanadium.

Non-condensable gas injection process

The reinjection of non-condensable gases is a new process. The gases are condensed and mixed with the geothermal water to be injected into a well. This process has the advantage of total elimination of H_2S but a careful evaluation of the influence of the injection of gases into the reservoir is necessary.

Peabody-Xertic process

H_2S is removed in this process by the Claus reaction in liquid media. A fraction of H_2S is absorbed in a solution of citric acid, the remainder H_2S is oxidized to SO_2. The H_2S in liquid phase and the SO_2 are mixed and the reaction produces elemental sulfur (Vancini, 1986).

Catalytic oxidation process

This process uses the Claus reaction in gas phase. Part of H_2S is oxidized to SO_2 with Fe_2O_3 as a catalyst, but the rest of the H_2S reacts with the SO_2 to produce elemental S.

Pressure swing adsorption process

This is a new method based on the selective adsorption of the H_2S by a porous media. This is an experimental process; the gas is, after desorption, treated by another method to transform the H_2S to elemental or harmless sulfur compounds.

H_2O_2/Iron chelate process

This method is used for cleaning the liquid from the condenser. The H_2S is oxidized with air and H_2O_2, using iron as the catalyst. The final product is soluble thiosulphates or sulfates. The installation cost of the process is low but the operation cost is high due to the consumption of chemicals.

Steam stripping

This process uses a stripping column for the contact with geothermal condensate and steam. This is a primary process, H_2S is transferred from liquid phase to a gas phase. Another process must be added to treat the gas coming out of the stripping column.

Burner-scrubber process

H_2S cleaning by this method can be used in the off-gas stream and also in the condensate stream. In the off-gas stream H_2S is burned to SO_2, then it is scrubbed with the condensate for the oxidation of H_2S to soluble thiosulphates.

BIOX process

The BIOX process is relatively new. In this process the off-gas is compressed and mixed with the condensate before the cooling tower. H_2S is converted to H_2SO_4 with the addition of the BIOX reactant.

Claus process

This process transforms the H_2S to sulfur in two steps. The first step is a partial oxidation with air at high temperatures (1000-1400°C); the products are: elemental sulfur, H_2S and SO_2. The second step is a catalytic reaction between H_2S and SO_2 to produce sulfur and water; the temperature in this second step is lower (200-350°C). The catalytic step is normally carried out in two or three stages. The sulfur recovery rate is close to 99.8%.

4.2.3 Detailed description of common processes for H₂S removal

Stretford process

The Stretford process, the LO CAT process and the Sulferox process, are most widely used for the H₂S cleaning in the geothermal industry. The main characteristic is the elimination of H₂S by oxidation. The general equation is

$$H_2S + \frac{1}{2}O_2 \rightarrow H_2O + S \tag{10}$$

The Stretford process consists of several steps. Figure 13 shows the scheme for the typical train of equipment and flow of material in this process.
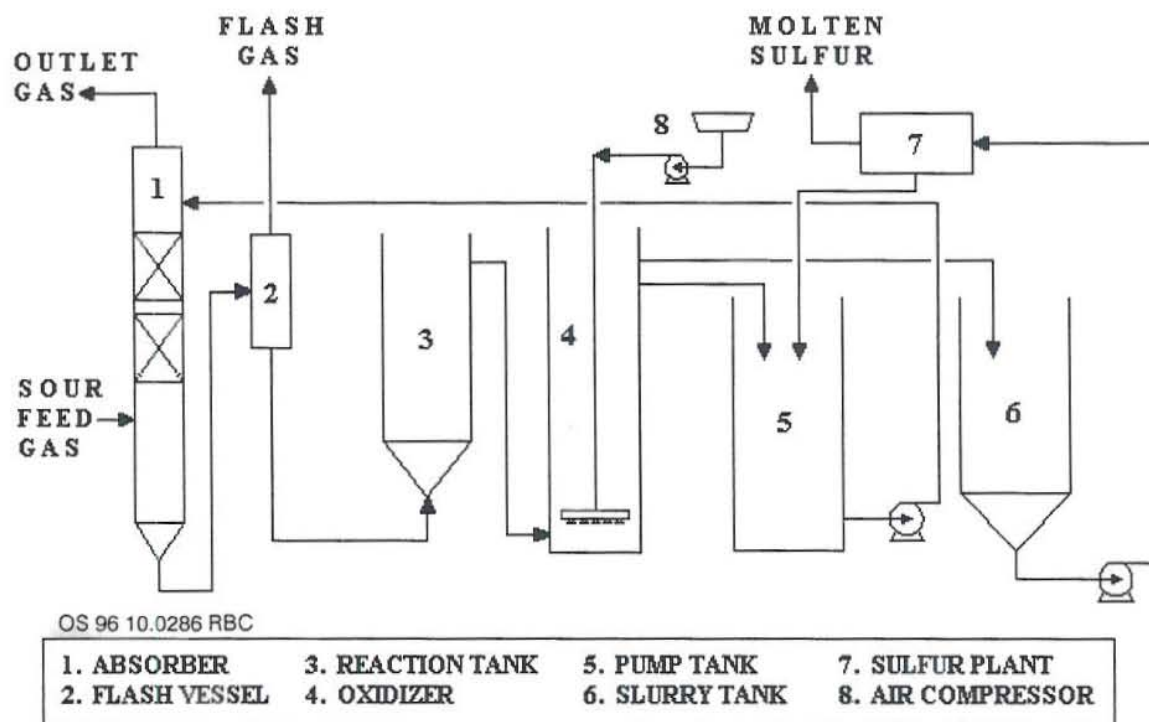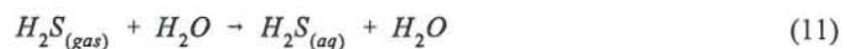

1. ABSORBER	3. REACTION TANK	5. PUMP TANK	7. SULFUR PLANT
2. FLASH VESSEL	4. OXIDIZER	6. SLURRY TANK	8. AIR COMPRESSOR

FIGURE 13: Scheme of the Stretford process (modified from Hardison, 1987)

The first step is the absorption of H₂S in an aqueous phase, following the equation

$$H_2S_{(gas)} + H_2O \rightarrow H_2S_{(aq)} + H_2O \tag{11}$$

The equipment used is an absorber, normally a packed tower to guarantee good contact between the liquid and the gas. The liquid phase is not composed only of H₂O, but also includes some of the chemicals from the oxidation and reoxidation processes. The liquid phase is received from the pump tank.

The absorption of the gas phase permits the ionization of H₂S in two different steps, according to the next set of equations:

$$H_2S(aq) \rightarrow H^+ + HS^- \tag{12}$$

$$HS^- \rightarrow H^+ + S^{2-} \tag{13}$$

This ionization is required for the subsequent oxidation of S^{2-}. Oxidation takes place in the reaction tank before the excess gas is delivered to the flash vessel.

The oxidation of the H_2S is represented as the reaction of the metavanadate ion, generally provided by the addition of sodium metavanadate to the reaction solution. The redox chemical equation is

$$2HS^- + 4VO_3^- + 2H_2O \rightarrow V_4O_9^{2-} + 2S + 4OH^- \tag{14}$$
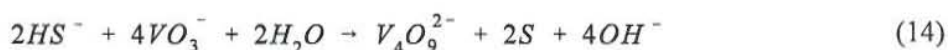
This reaction is relatively slow with a residence time close to 15 minutes (Hardison, 1987). For this reason, greater concentrations of vanadium are required to keep the size of the reaction tank within commercial sizes.

The next stage is the reoxidation of the vanadium, which is carried out by the addition of the sodium salt of the 2:7 isomer of anthraquinone disulfonic acid (ADA) and O_2. The chemical reaction is represented by
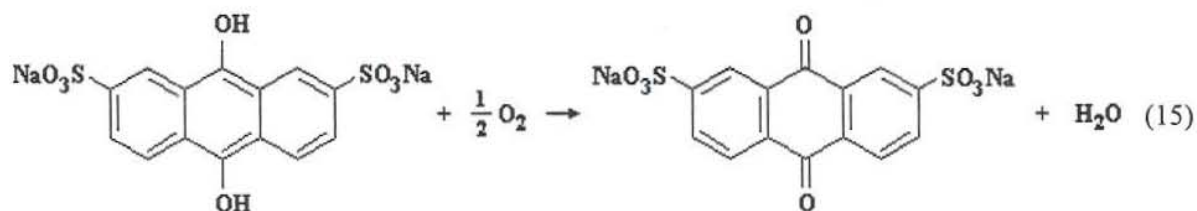
The help of the ADA in the reoxidation of the vanadium salt is provided by the equation:

$$2V_4O_9^{-2} + 2OH^- + H_2O + 2ADA(oxid) \rightarrow 4VO_3^- + 2ADA.2H^- \tag{16}$$
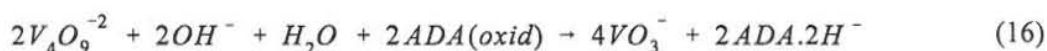
These reactions take place in the oxidizer tank. The reaction rates of reactions 6 and 7 are relatively slow. This factor, in addition to the slow transfer of the O_2 from the air pumped to the liquid media, makes the retention time long for this stage of the process (Hardison, 1987).

The second use of the oxidation tank is the separation of sulfur by flotation. This process is carried out by the same air used to feed O_2. The flotation process creates froth in the top and a liquid phase in the bottom of the oxidizer. The separation of these two phases is carried out in two different tanks. The first one is called the pump tank, which stores the liquid phase pumped to the packed tower to absorb the H_2S. The second is the slurry tank, used for the accumulation of the sulfur froth, generally close to 5% wt of the sulfur. Finally, the aerated froth goes to the sulfur plant where commercial sulfur is produced. The clean CO_2 leaves the process in the absorber as outlet gas steam.

The problem with the Stretford process is the size of the tanks and also the retention time required for the different reactions. The use of vanadium compounds creates a problem in waste disposal, owing to environmental regulations. The consumption of the ADA is problematic, due to the biological activity and contamination of thiosulphate byproducts, which provoke the discard of reactive solutions and also the loss of chemicals (Vancini and Althen, 1985).

LO CAT process

The LO CAT process is basically a simplification of the Stretford process; the principal variation is the utilization of iron as the redox agent, in place of the vanadium, for the oxidation of H_2S. Some good characteristics of the iron are: high reaction rate, environmental compatibility and low price. The principal problem is its low solubility in water. For this reason, the utilization of organic chelating agents is required to accomplish the reaction.

The oxidation reaction is the same as shown in Equation 10, but the specific oxidation reaction is represented by the following equation:

$$S^= + 2Fe^{+++} \rightarrow S + 2Fe^{++}. \tag{17}$$

There are two basic operative differences between the LO CAT and the Stretford process. First, in the LO CAT process, the reaction occurs directly after the injection of air. In comparison with the Stretford process, this corresponds to the use of the oxidizer as a reaction tank, suppressing the last one. Second, the separation of the sulfur is by settling. This change permits the production of a sulfur slurry with 10-20% wt directly in the oxidizer, and the elimination of the pump and slurry tanks. Figure 14 shows the simplifications in the LO CAT process, and Figure 15 shows the typical LO CAT process.
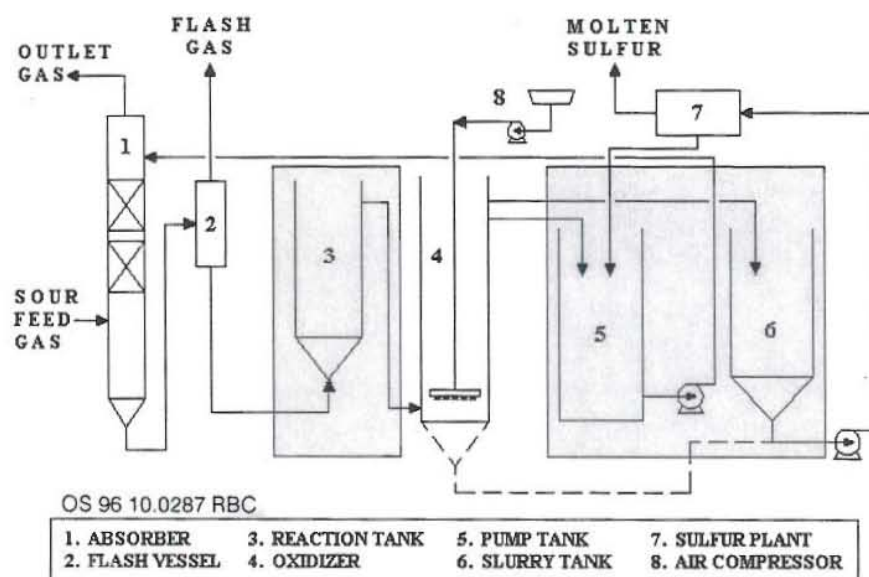

| 1. ABSORBER | 3. REACTION TANK | 5. PUMP TANK | 7. SULFUR PLANT |
| 2. FLASH VESSEL | 4. OXIDIZER | 6. SLURRY TANK | 8. AIR COMPRESSOR |

FIGURE 14: Scheme of the simplification of the Stretford process in the LO CAT process (modif. from Hardison, 1987)

The reduction in the equipment allows the fabrication of cleaning plants at lower cost, with fewer problems with biological activity and the formation of thiosulphate byproducts, making the LO CAT process a good option for H_2S abatement (Henderson and Dorighi, 1989).

Sulferox process

The Sulferox process removes H_2S by oxidation with iron as a catalyst agent. The chemical reactions are the same as in the LO CAT process, represented by Equation 17. The main difference between the LO CAT and the Sulferox processes is in the treatment of the fluids after the absorption and reaction; and also in the regeneration of the iron. For the separation of sulfur, the Sulferox process filter is used.

The product is a cake with a low water content in comparison with the sulfur slurry produced in the oxidizer of the LO CAT process. The general flow diagram for the Sulferox process is shown in Figure 16.
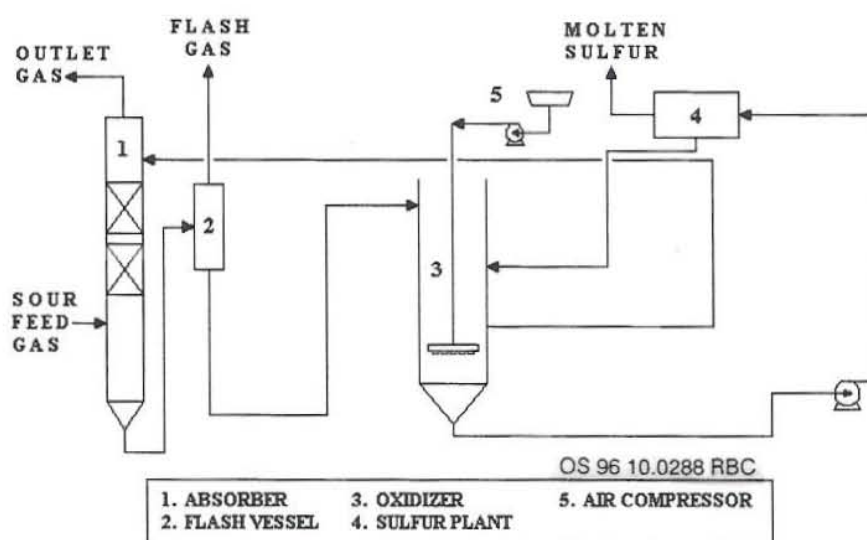

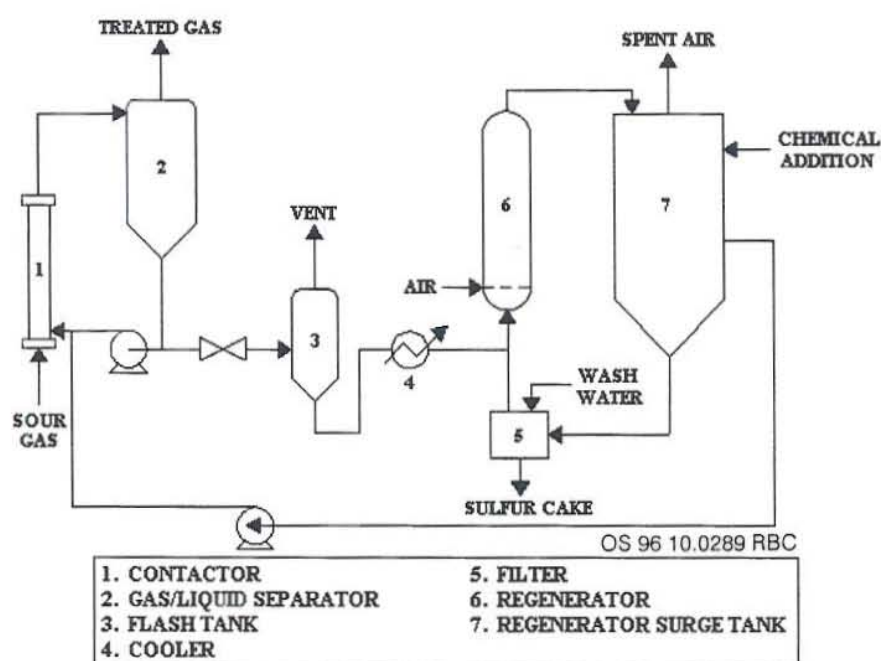FIGURE 15: Scheme of the LO CAT process (modified from Hardison, 1987)

FIGURE 16: Scheme of the Sulferox process

Pressure swing adsorption process
The pressure swing process is based on the adsorption of the H_2S by an inorganic porous medium, for example zeolite or alumina. The H_2S in the non-condensable gas is adsorbed selectively at high pressure; afterwards, it is desorbed by a drop in pressure.

A scheme of the process is shown in Figure 17 (Hirowatari et al., 1995). In this process, the non-condensable gases are transported through the adsorption-desorption columns. The gas with high H_2S concentration is conducted to the combuster and converter to produce SO_2 and SO_3, and after these, the sulfur oxides react with water in the scrubber to finally obtain H_2SO_4.

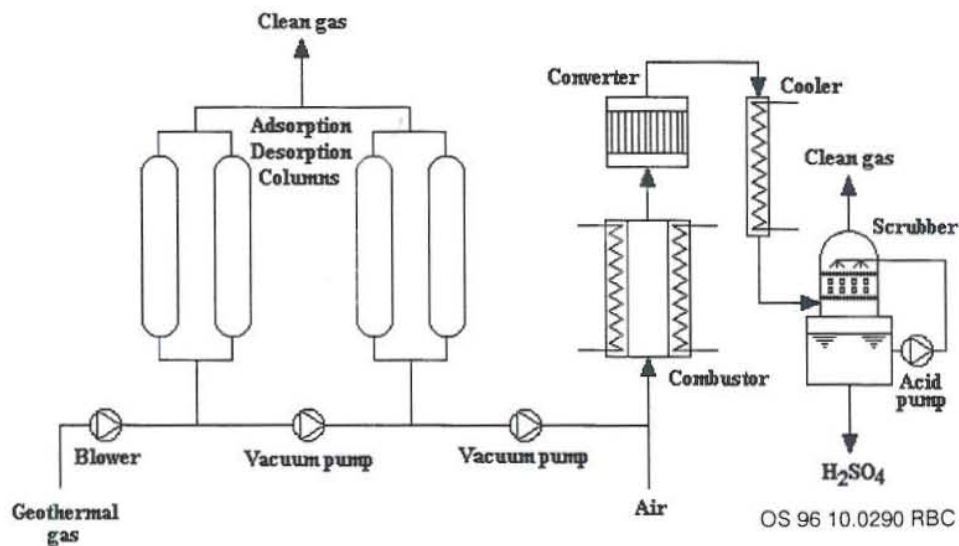FIGURE 17: Scheme of the pressure swing adsorption process
(modified from Hirowatari et al., 1995)

5. HAEDARENDI, ICELAND, AND KIZILDERE, TURKEY, GEOTHERMAL FIELDS

5.1 The Haedarendi CO_2 plant

A plant for the production of CO_2 is in operation at the Haedarendi geothermal field in Iceland. The field has an intermediate temperature and relatively high gas content, 1.25% by weight. With the high concentration of CO_2 and low concentrations of H_2S (350 ppm), a plant for the production of liquid CO_2 was installed in 1986. The production is close to 550 tons per year of liquid CO_2.
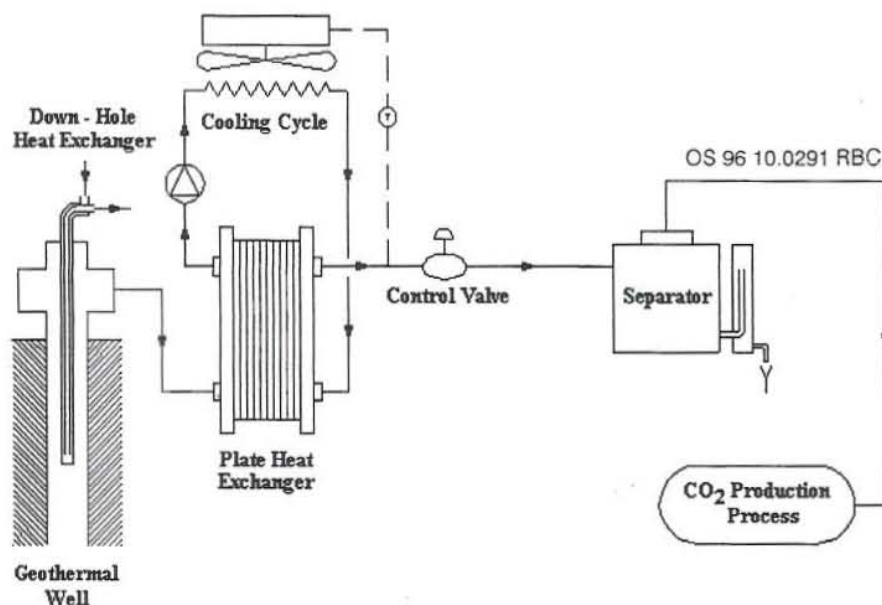

The principal problem in the exploitation of this field is calcite scaling. To avoid this problem a special device is used based on a down-hole heat exchanger; the scheme for this device is shown in Figure 18.

The process for the production of CO_2 in Haedarendi is basically composed of four stages: cleaning, compression, dehumidification and storage. A diagram of the process is shown in Figure 19.
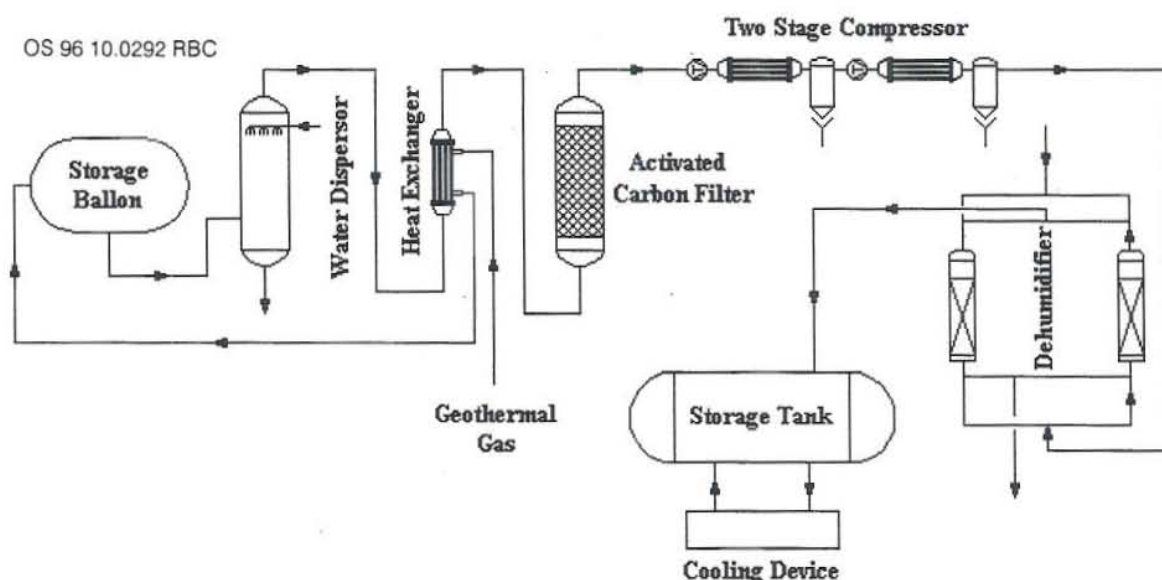
FIGURE 18: Scheme of the system for mitigation of scaling at Haedarendi

FIGURE 19:   Scheme of the liquid CO2 production process at Haedarendi

First, the gas from the well is stored in the balloon. This balloon is used as a regulator of the raw gas for the process. The cleaning of the gas begins in the water disperser, the objective being the washing of the gas and the condensation of some water in the gas due to a decrease in temperature. The activated carbon filter removes the remaining H_2S.

Compression is carried out in a two stage compressor with cooling and condensate traps after each stage. The final compression pressure is 15 bar-g. The drying process is carried out in a packed column with silica gel, using a second column for the regeneration cycle. For the storage of liquid CO_2, a tank is provided with a cooling system to keep the temperature close to -30°C.

5.2 Kizildere geothermal field

Another example of liquid CO_2 production is the CO_2 plant in Kizildere, Turkey. In this field, a plant producing 30,000 tons per year of liquid CO_2 has been installed. The plant utilizes the non-condensable gases from the 20 MW power plant (Simsek, 1985).

The gas containing 95% CO_2 and small quantities of H_2S and N_2, is sent to the CO_2 plant, where the H_2S is eliminated. Later, the gas is cooled by the geothermal absorption freezing system upon compression to a liquid state. A minor quantity of nitrogen is bled off. The product is 99.9% CO_2 (Líndal, 1996, personal communication).

6. CONCLUSIONS

1.   The production of liquid CO_2 from geothermal sources is technically feasible and economically viable. Haedarendi geothermal field, with a production of approximately 500 tons per year and Kizildere geothermal field, with 30,000 tons per year, are prime examples.

2.   Technically, the CO_2 from the 60 MW Miravalles geothermal power plant is a potential source

for the commercial production of liquid CO_2.

3.   Cleaning the gas decreases the emanation to the atmosphere of gases like H_2S and also CO_2, and improves environmental conditions when exploiting geothermal resources.

4.   The presence of toxic gases in the geothermal gas makes necessary the utilization of special elimination processes. H_2S removal in two stages for food grade purification is recommended. The primary abatement process is to reduce the H_2S normally to 99.9%. For this first treatment, the redox process should be considered, due to its wide application in industry. For the second H_2S abatement process activated carbon filtration in a packed tower or a scrubbing tower with a solution of potassium permanganate is recommended.

ACKNOWLEDGEMENTS

REFERENCES

Ármannsson, H., Gíslason, G., and Hauksson, T., 1982: Magmatic gases in well fluids aid the mapping of the flow pattern in a geothermal system. *Geochim. Cosmochim. Acta, 46,* 167-177.

Ármannsson, H., and Kristmannsdóttir, H., 1992: Geothermal environmental impact. *Geothermics, 21-5/6,* 869-880.

Arnórsson, S., and Gunnlaugsson, E., 1985: New gas geothermometers for geothermal exploration - calibration and application. *Geochim. Cosmochim. Acta, 49,* 1307-1325.

Arnórsson, S., Björnsson, S., Muna, Z.W., and Bwire-Ojiambo, S., 1990: The use of gas chemistry to evaluate boiling processes and initial steam fractions in geothermal reservoirs with an example from the Olkaria field, Kenya. *Geothermics, 19-6,* 497-514.

Buse Anlagenbau: *Technical brochures.*

Darling, W.G., Griesshaber, E., Andrews, J.N., Armannsson, H., and O'Nions, R.K., 1995: The origin of hydrothermal and other gases in the Kenya Rift Valley. *Geochim. Cosmochim. Acta, 59,* 2501-2512.

Ferguson P.A., 1975: *Hydrogen sulfide removal from gases, air and liquids.* Noyes Data Corporation,

Park Ridge, New Jersey, 348 pp.

Giggenbach, W.F., 1980: Geothermal gas equilibria. *Geochim. Cosmochim. Acta, 44,* 2021-2032.

Giggenbach, W.F., 1991: Chemical techniques in geothermal exploration. In: D'Amore, F. (co-ordinator), *Application of geochemistry in geothermal reservoir development.* UNITAR/UNDP Publication, Rome, 119-142.

Hardison, L.C., 1987: H₂S emission control by chelated iron scrubbing; an environmentally sound alternative to Stretford. *Geoth. Res.Council, Transactions, 11,* 123-128.

Henderson, J.M., and Dorighi, G.P., 1989: Operating experiences of converting a Stretford to a LO-CAT® H₂S abatement system at Pacific Gas and Electric Company's Geysers Unit 15. *Geoth. Res. Council, Transactions, 13,* 593-595.

Hirowatari, K., Kusaba, S., Izumi, J., and Takeuchi, K., 1995: Production of sulfuric acid from geothermal power station exhausted gas for use in scale prevention. *Proceedings of the World Geothermal Congress 1995, Florence, Italy, 4,* 2445-2450.

Michels, D.E., 1979: Reaction mechanisms associated with CaCO₃ scale and release of CO₂ East Mesa. *Geoth. Res. Council, Transactions, 3,* 457-460.

Quintero M.N., 1987: A potential remotion process and utilization of the non-condensable gases CO₂ and H₂S from the geothermal wells in Cerro Prieto. *Geoth. Res.Council, Transactions, 11,* 143-148.

Sanopoulos, D., and Karabelas, A., 1995: H₂S abatement in geothermal plants - evaluation of process alternatives. *Proceedings of the World Geothermal Congress 1995, Florence Italy, 4,* 2785-2789.

Simsek, S., 1985: Present status and future development of the Denizli-Kizildere geothermal field of Turkey. *International Symposium on Geothermal Energy, Geoth. Res. Council, Transactions, 9,* 203-210.

Union Construction: *Technical brochures.*

Vancini, C., 1986: Peabody - Xertic, a new process to desulphurise geothermal non-condensable gas streams. *Geoth. Res. Council, Transactions, 10,* 293-298.

Vancini, C. and Althen, H., 1985: Optimization of Peabody-Stretford process and operation. *Geoth. Res. Council, Transactions, 9-II,* 273-278.

Zhao Ping, and Ármannsson, H., 1996: Gas geothermometry in selected Icelandic geothermal fields with comparative examples from Kenya. *Geothermics, 25-3,* 307-347.

APPENDIX 1: Emanations of CO$_2$ and H$_2$S for different types of power plants showing the Krafla and Miravalles geothermal power plants (Ármannsson and Kristmannsdóttir, 1992)

Type of power plant	Gas emanations (g/kWh)	
	CO$_2$	H$_2$S
Coal	1000	11
Oil	850	11
Gas	550	0.005
Krafla	96	6
Miravalles	54	0.41

APPENDIX 2: Composition of non-condensable gases for eight different fields

Geothermal field	Gas composition (% weight)				
	CO$_2$	H$_2$S	N$_2$	H$_2$	CH$_4$
Olkaria (Kenya)[c,d,f]	80.67	9.28	1.72	7.68	0.65
Wairakei (New Zealand)[e]	88.67	10.02	0.80	0.24	0.25
Ngawha (New Zealand)[e]	95.88	1.01	0.30	0.28	2.52
Zunil (Guatemala)[e]	96.24	2.51	0.80	0.43	0.02
Miravalles (Costa Rica)[e]	98.24	0.60	0.80	0.33	0.03
Svartsengi (Iceland)[b]	92.54	2.32	4.98	0.10	0.06
Hveragerdi (Iceland)[b,f]	75.32	7.11	15.80	1.62	0.15
Krafla (Iceland)[a,b,f]	86.16	9.29	2.62	1.87	0.06

a: Ármannsson et al., 1982
b: Arnórsson and Gunnlaugsson, 1985
c: Arnórsson et al., 1990
d: Darling et al., 1995
e: Giggenbach, 1980
f: Zhao Ping and Ármannsson, 1996