



## **PRELIMINARY STUDY ON EMISSION ABATEMENT AND USE OF GAS FROM GEOTHERMAL POWER PLANTS IN EL SALVADOR**

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### **ABSTRACT**

Geothermal energy is regarded worldwide as a clean and renewable energy source. Electricity production using geothermal resources is much more environmentally favourable than the combustion of fossil fuels; however, gas emission is regarded as one of the most important environmental impacts of geothermal energy production and must be handled with special care.

The environmental and economic effects of the treatment of gas emitted from the Berlín geothermal power plant were studied. Different methods for gas emission abatement were reviewed and an economical assessment for the application of a H<sub>2</sub>S removal and CO<sub>2</sub> cleaning process was carried out.

It was found that carbon dioxide and hydrogen sulphide can be successfully treated for elemental sulphur recovery and purified liquid carbon dioxide production. Environmental impacts such as global warming, acidification of rain and soil would be reduced by using the geothermal non-condensable gases instead of releasing them to the atmosphere; attractive incomes can be generated by selling liquid CO<sub>2</sub> and carbon certified emission reduction credits.

### **1. INTRODUCTION**

Geothermal energy production is expected to increase in El Salvador. Since it is environmentally friendly and an indigenous resource, it would help to reduce petroleum dependency. Environmental and economical advantages of geothermal energy could be enhanced with the application of abatement technologies and the recovery of by-products from “wastes”, such as geothermal non-condensable gases, generated in the electricity production process.

Carbon dioxide and hydrogen sulphide are proportionally the highest components in geothermal non-condensable gases (NCG), typically 90-98% and 2-10% by weight, respectively. Others gases with very low concentrations include nitrogen, hydrogen, oxygen, argon and methane. The amount of NCG in the steam depends on the special characteristics of the reservoir; typical concentrations are in the range of 0.5 to 5% by weight.

This report includes a characterization of gas emissions for both of the geothermal power plants currently in operation in El Salvador; a brief description of some international regulations for gas emissions; characteristics of the market for by-products generated by gas treatment; an overview of some available methods for H<sub>2</sub>S removal and CO<sub>2</sub> recovery, and an economical assessment for the application of gas treatment technologies in the Berlín geothermal power plant. This project was carried out as part of 6 months training at the Geothermal Training Programme of the United Nations University in 2007.

## 2. EMISSION OF GASES FROM GEOTHERMAL POWER PLANTS IN EL SALVADOR

### 2.1 General geothermal background of El Salvador

El Salvador is located in Central America close to the “Pacific Rim” where large amounts of active volcanoes and geothermal areas are located (Rivas, 2000). The source of geothermal potential in El Salvador is the subduction of the Cocos plate under the Caribbean plate, as part of the “ring of fire”. The subduction zone causes a volcanic chain that trends WNW-ESE through the middle of the country. Areas of geothermal potential are found around the volcanoes: the heat sources are the magma chambers, the structures are calderas or grabens associated with volcanic activity (mostly quaternary, but some tertiary), and the reservoirs are formed by rainwater infiltration into the high part of the volcanic craters (Rodríguez and Herrera, 2005).

There are two geothermal fields in El Salvador that have operating power plants, Ahuachapán and Berlín, both owned and operated by LaGeo, a spinoff privatized company of the government electric utility (Figure 1). In 2007, their combined installed capacity is rated at 195.2 MW. The Ahuachapán geothermal field, in the western part of the country, has been exploited over the last 32 years; it was one of the first geothermal resources utilized to produce power for a developing country. The Berlín field is located in the eastern part of El Salvador and started commercial operations in 1992.

At present, there are exploration and resource evaluation projects in two other fields: San Vicente and Chinameca, located in the central and eastern parts of the country, respectively, where potentially new

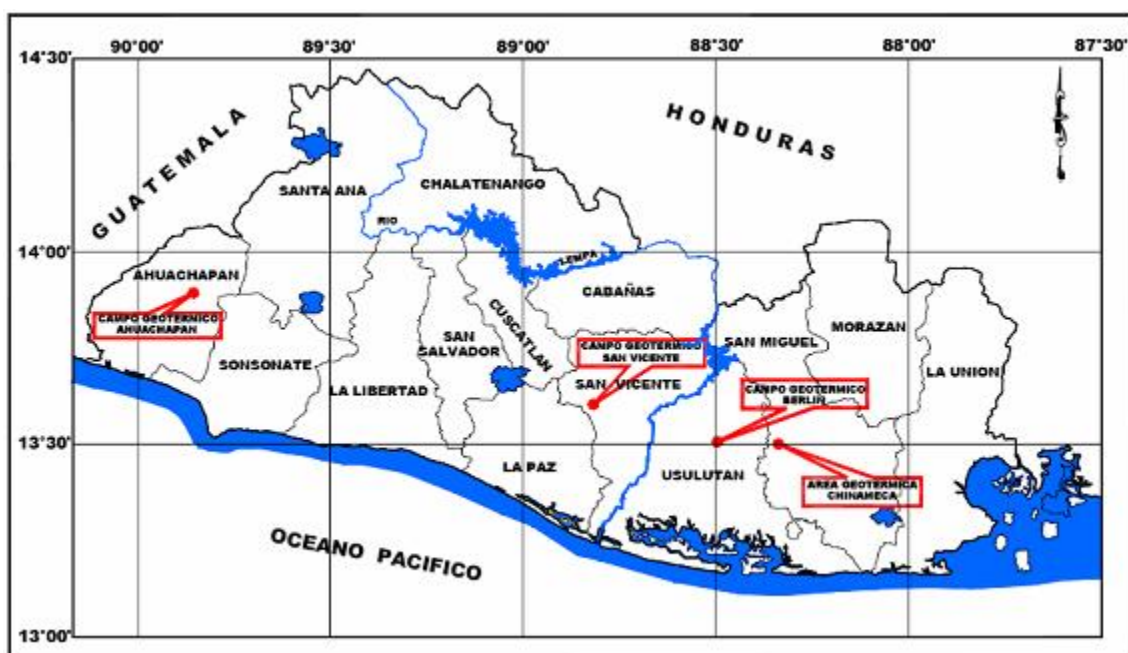


FIGURE 1: Geothermal fields in El Salvador (modified from Rodríguez and Herrera, 2005)

geothermal power plants could be constructed as a result of successful exploration. The locations of the geothermal fields in El Salvador are shown in Figure 1.

## 2.2 Current emissions of carbon dioxide and hydrogen sulphide

The characteristics of the reservoirs in both Salvadorian geothermal fields currently in production are quite different and, therefore, parameters like flowrate and composition of NCG are different (see Table 1).

TABLE 1: Characterization of NCG in geothermal power plants in El Salvador

Parameter	Berlín	Ahuachapán
Installed capacity (MW)	100	95
NCG flow rate (kg/h)	3600	2664
% wt of CO <sub>2</sub> in NCG	91.1	95.8
% wt of H <sub>2</sub> S in NCG	7.9	3.4
% wt of other gases	1.0	0.8
CO <sub>2</sub> emission rate (kg/h)	3025	2468
H <sub>2</sub> S emission rate (kg/h)	311	79

Gas emissions from both geothermal power plants in El Salvador are relatively low compared to gas emissions from some geothermal power plants in Iceland and from typical power plants burning fossil fuels (see Table 2).

TABLE 2: Gas emissions from geothermal and fossil fuel power plants

Power plant	Electric power capacity in 2005 (MW)	CO <sub>2</sub> emission (tons/year)	H <sub>2</sub> S emission (tons/year)	CO <sub>2</sub> emission (kg/MWh)	H <sub>2</sub> S emission (kg/MWh)
Berlín <sup>1</sup>	100	26499	2725	30	3.1
Ahuachapán	95	21620	692	26	0.8
Krafla	100	101400	6000	116	6.8
Bjarnarflag	90	19200	8700	24	11.0
Nesjavellir <sup>2</sup>	120	15400	6730	15	6.4
Hellisheidi <sup>1</sup>	120	57000	11000	24	4.6
Svartsengi <sup>2</sup>	46.4	57676	820	142	2.0
Reykjanes <sup>1</sup>	100	47300	1100	54	1.2
Natural gas				599	
Petroleum				893	
Coal				950	

<sup>1</sup> In 2007

<sup>2</sup> These plants also produce hot water for district heating. Here, all the emissions are attributed to electric energy production.

In Berlín and Ahuachapán power plants, one ejector system is used to extract gas from the condenser; then it is piped to the cooling tower fans and mixed with the steam plume (Figure 2) which allows a good dispersal of the gas into the atmosphere.

Measurements of H<sub>2</sub>S and CO<sub>2</sub> concentrations in the air have been carried out in Berlín and Ahuachapán power plants and their vicinities twice a year; see results for the Berlín power plant in Figure 3. The results reveal that the concentrations of both gases are far lower than the standards issued by international organizations and, therefore, there are no health risks to workers and neighbours of the power plants.



FIGURE 2: Emission of gas mixed with steam in the Berlín geothermal power plant

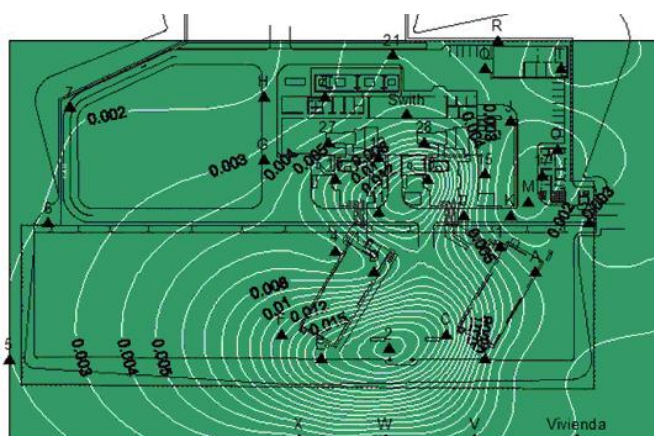


FIGURE 3: Contour lines of H<sub>2</sub>S concentration in the Berlín power plant (Franco, 2006)

Gas abatement is not needed at present in the Salvadorian operating power plants. However, economic and environmental benefits of recovery and use of the gas, instead of releasing it to the atmosphere, should be evaluated for new power plants to be constructed in the near future.

### 2.3 Berlín power plant as a case study

As mentioned above, two new geothermal power plants could be constructed in the next few years as a result of successful exploration in the San Vicente and Chinameca fields. In order to make a preliminary evaluation of the different methods which could be used for gas abatement in new geothermal power plants in El Salvador, data from the Berlín power station will be used; the NCG flowrate is higher there than in Ahuachapán.

Power production in Berlín geothermal field started in February 1992 when two 5 MW back pressure units went on line. In 1999, two 28 MW condensing units were commissioned and the previous units were disconnected. In December 2006, an additional 44 MW unit was installed, bringing the total installed capacity to 100 MW (Rodríguez and Herrera, 2007).

TABLE 3: Composition of NCG emitted from the Berlín power plant

Component	Gas from the condenser (%wt)
CO <sub>2</sub>	91.0
H <sub>2</sub> S	7.9
N <sub>2</sub>	0.99
H <sub>2</sub>	0.026
O <sub>2</sub>	0.014
Ar	0.011
CH <sub>4</sub>	0.0051
Total	99.9

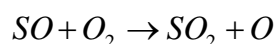
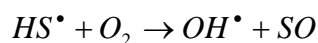
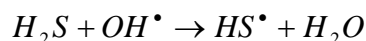
To date, 39 wells have been drilled in the Berlín field, 14 production wells and 19 injectors; 6 wells have been abandoned (TR-1, TR-6, TR-11/B/C, TR-10A). The total steam flowrate is 215-220 kg/s and the injected brine is around 550-560 kg/s. Therefore, the total mass extracted is around 775 kg/s (Rodríguez and Herrera, 2007).

The composition of the NCG emitted into the atmosphere from the Berlín power plant contains about 91% by weight of CO<sub>2</sub> and about 8% by weight of H<sub>2</sub>S (see Table 3). This data will be used in Section 7 as an input for cost estimation of gas emission abatement and earnings for the sale of generated by-products.

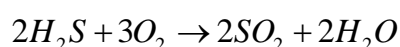
### 2.4 Behaviour of the gases in the atmosphere

The effect of CO<sub>2</sub> released into the atmosphere is well known; this gas is regarded as the principal greenhouse gas, responsible for global warming. Once released to the atmosphere, H<sub>2</sub>S may be

oxidized to SO<sub>2</sub> and sulfate compounds; this conversion is believed to be dependent on the atmospheric and weather conditions and the concentrations of ozone and OH radicals. The following chemical reactions take place in the conversion of H<sub>2</sub>S to SO<sub>2</sub> (Manahan, 1991):



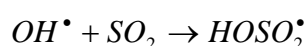
Thus, the overall reaction is:



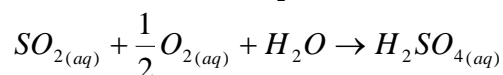
According to Kristmannsdóttir et al. (2000), due to atmospheric conditions in Iceland, only a minor fraction of the H<sub>2</sub>S released from the Nesjavellir geothermal field is converted to SO<sub>2</sub>; the study claims that precipitation effectively washes H<sub>2</sub>S from the air.

The life-time of H<sub>2</sub>S in the air is expected to range from 2 hours to 42 days. A residence time of approximately 1.7 days at an ozone concentration of 0.05 mg/m<sup>3</sup> has been calculated. The effective life-time for hydrogen sulfide, based on summer daytime and yearly average hydroxyl radical concentrations, have been estimated to be 0.23 and 2.3 days, respectively. Life-times in the air, ranging from approximately 1 day in the summer to 42 days in the winter (in the USA), have been estimated (ATSDR, 2006).

Sulphur dioxide in the atmosphere ultimately is oxidized to sulphuric acid and sulphate salts; many factors, including temperature, humidity, light intensity, atmospheric transport and surface characteristics of particular matter, may influence the atmospheric chemical reactions of SO<sub>2</sub> (Manahan, 1991). Therefore, contributing to the formation of acid rain is one of the environmental impacts associated with SO<sub>2</sub>. One of the chemical reactions that can take place in the atmosphere is:

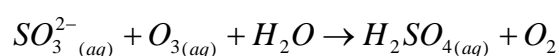
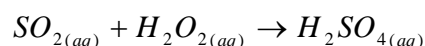


The free radical formed in this reaction is eventually converted to a form of sulphate. The reaction between SO<sub>2</sub> and dissolved molecular O<sub>2</sub>:



is considered to be insignificant in the absence of catalytic species.

The reactions of SO<sub>2</sub> with hydrogen peroxide and ozone are considered to be more important:



The conversion rate of H<sub>2</sub>S to SO<sub>2</sub>, considering the atmospheric conditions in the Salvadorian geothermal fields, has not been studied; a better knowledge of the behaviour of the H<sub>2</sub>S in this area is needed.

### 3. REGULATIONS FOR GAS EMISSIONS

#### 3.1 Environmental issues

Worldwide tendencies, including debates and conferences on the environment (Rio and Kyoto), have contributed to the search for a legal framework and formal organizational structure to protect the environment and to improve the standard of living, particularly in developing countries (Arévalo, 2006). Regulations related to hydrogen sulphide emissions are nowadays quite stringent in Europe and North America and are starting to evolve in Pacific Rim countries. For carbon dioxide, the principal greenhouse gas, emission limits in developed countries were established in the Kyoto Protocol.

In 1997, the Ministry of Environment and Natural Resources of El Salvador (MARN) was created as a governing institution and focused on the agreements, conventions and protocols of the United Nations. The vision of this institution is “to direct an effective environmental management through policies and norms and facilitate the sustainable development for Salvadorian society”. The environmental law in El Salvador was made official in 1998, while the national environmental policy and benefits of natural resources (water, air, biodiversity, etc) were declared official in 2000. All of these became legalized instruments for the public sector to rely upon for environmental management (Arévalo, 2006).

At present, in El Salvador there are no regulations of gas emissions applied to geothermal power plants; however, trends on world emission regulations for H<sub>2</sub>S indicate that they are becoming even more stringent. New geothermal power plants have to be able not only to achieve these standards but also be compatible with other industries in the area, like tourism, and be accepted by the communities hosting the plants.

#### 3.2 Safety and health issues

Hydrogen sulphide is regarded as poisonous in high concentrations and has an unpleasant smell even at very low concentrations. Carbon dioxide, a constituent of exhaled air, is hazardous in high concentrations.

Hydrogen sulphide can be hazardous to workers in the gas, oil chemical, geothermal energy, and viscose rayon industries and to workers in sewer systems, tanneries, mining, drilling, smelting, animal-waste disposal, and on fishing boats (Weil et al., 2006). People usually can smell hydrogen sulphide at low concentrations in the air, ranging from 0.0005 to 0.3 parts per million (ppm) (0.0005–0.3 parts of H<sub>2</sub>S in 1 million parts of air); however, at high concentrations, a person might lose the ability to smell it. This can make hydrogen sulphide very dangerous.

Exposure to low concentrations of H<sub>2</sub>S may cause irritation to the eyes, nose, or throat. It may also cause difficulties in breathing for some asthmatics. Brief exposures to high concentrations of hydrogen sulphide (greater than 500 ppm) can cause a loss of consciousness. In most cases, the person appears to regain consciousness without any other effects. However, in some individuals, there may be permanent or long-term effects such as headaches, poor attention span, poor memory, and poor motor function (ATSDR, 2006).

In the United States, the Environmental Protection Agency (EPA), the Occupational Safety and Health Administration (OSHA), and the Food and Drug Administration (FDA) are federal agencies that develop regulations for toxic substances, including hydrogen sulphide. The Agency for Toxic Substances and Disease Registry (ATSDR) and the National Institute for Occupational Safety and Health (NIOSH) are two federal organizations which give recommendations for toxic substances. Recommendations and regulations are also updated periodically as more information becomes available. Some regulations and recommendations for hydrogen sulphide include:

- OSHA has established an acceptable ceiling concentration of 20 ppm for hydrogen sulphide in a workplace, with a maximum level of 50 ppm allowed for 10 minutes maximum duration if no other measurable exposure occurs.
- NIOSH has set a maximum Recommended Exposure Limit (REL) ceiling value of 10 ppm for 10 minutes maximum duration.

In El Salvador, there are no regulations for H<sub>2</sub>S and CO<sub>2</sub> concentrations in a workplace; international guidelines are followed.

A more complete listing of regulations and recommendations issued by international agencies and organizations is shown in Table 4. Up to a 0.5% volume of carbon dioxide in the air is not considered harmful, but this gas concentrates in low spots as it is one and one-half times heavier than air. Five percent volume of carbon dioxide in the air causes a threefold increase in the breathing rate, and prolonged exposure to concentrations higher than 5% may cause unconsciousness and death. Ventilation sufficient to prevent the accumulation of dangerous percentages of carbon dioxide must be provided where carbon dioxide gas has been released or dry ice has been used for cooling. The ACGIH TLV (TWA) is 5000 ppm (9000 mg/m<sup>3</sup>) with a STEL of 30,000 ppm (54,000 mg/m<sup>3</sup>). The National Institute for Occupational Safety and Health has recommended a TWA of 5000 ppm as a limit, with short-term excursions up to 3% (30,000 ppm) for 10 minutes (Pierantozzi, 2003).

## 4. MARKET FOR SULPHUR AND CARBON DIOXIDE BY-PRODUCTS

### 4.1 Sulphur

Sulphur has been known since antiquity. Early humans used sulphur to colour cave drawings, employed sulphur fumes to kill insects and to fumigate, and knew about sulphur's colour-removing or bleaching action. Antique cultures believed sulphur to have mystical powers and medicinal properties. The first commercial sulphur was produced in Italy early in the fifteenth century and sulphur production became Italy's main industry in 1735. In the United States, H. Frasch conceived of melting the sulphur underground by injecting superheated water into the formation and then lifting the melted sulphur to the surface using a sucker-rod pump. In 1902, the Frasch process was successfully commercialized (Kirk-Othmer, 2006).

#### *Supply/demand*

Sulphur is produced from a variety of sources using many different techniques in many countries around the world. Sources are called voluntary if the sulphur is considered to be the principal, and often the only, product. Sulphur has also been recovered as a by-product from various process operations. Today, sulphur recovered as a by-product, accounts for a larger portion of the world supply than does mined or voluntary material. Sulphur is obtained from hydrogen sulphide, which evolves when natural gas, crude petroleum, tar sands, oil shale, coal, and geothermal brines are desulphurized. Other sources of sulphur include metal sulphides such as pyrites; sulphate materials, including gypsum; and elemental sulphur in native and volcanic deposits mined in the traditional manner (Kirk-Othmer, 2006).

Of greater significance today is the recovery of elemental sulphur from crude oil refineries as the sulphur content of crude oils has increased and as regulations on the sulphur content of oil and gasoline products have become increasingly stringent (Suresh, 2006). According to Suresh (2006), the world sulphur production in 2004 was approximately 68 million metric tons, see Figure 4, with an estimated fob value of about \$1.6 billion. An annual growth rate of about 2.8% of the world's production of elemental sulphur is expected during the forecast period (1985-2010). The supply/demand situation is projected to be relatively tight for the next couple of years with remelts from inventories utilized to supply requirements. Figure 4 shows the world supply and demand for sulphur in all its forms.

TABLE 4: International guidelines for H<sub>2</sub>S exposure limits

Agency	Description	Information	Reference
WHO	Air quality guideline (averaging time of 24 hours)	0.15 mg/m <sup>3</sup>	WHO 2000
ACGIH	TLV (8-hour TWA) STEL	10 ppm <sup>a</sup> 15 ppm <sup>a</sup>	ACGIH 2005
EPA	Interim AEGL-1 <sup>b</sup> <i>10 minutes</i> <i>30 minutes</i> <i>60 minutes</i> <i>4 hours</i> <i>8 hours</i> Interim AEGL-2 <sup>c</sup> <i>10 minutes</i> <i>30 minutes</i> <i>60 minutes</i> <i>4 hours</i> <i>8 hours</i> Interim AEGL-3 <sup>d</sup> <i>10 minutes</i> <i>30 minutes</i> <i>60 minutes</i> <i>4 hours</i> <i>8 hours</i>	0.75 ppm 0.60 ppm 0.51 ppm 0.36 ppm 0.33 ppm  41 ppm 32 ppm 27 ppm 20 ppm 17 ppm  76 ppm 59 ppm 50 ppm 37 ppm 31 ppm	EPA 2006
NIOSH	REL (10-minute ceiling TWA) IDLH	10 ppm  100 ppm	NIOSH 2006
OSHA	Acceptable ceiling concentration (8 hours)	20 ppm	OSHA 2006 29CFR1910.1000, Table Z-2

<sup>a</sup> Notice of intended changes: adopted values are those for which changes are proposed.

<sup>b</sup> AEGL-1 is the airborne concentration of a substance above which it is predicted that the general population, including susceptible individuals, could experience notable discomfort, irritation, or certain asymptomatic non-sensory effects. However, the effects are not disabling and are transient and reversible upon cessation of exposure.

<sup>c</sup> AEGL-2 is the airborne concentration of a substance above which it is predicted that the general population, including susceptible individuals, could experience irreversible or other serious, long lasting adverse health effects or an impaired ability to escape.

<sup>d</sup> AEGL-3 is the airborne concentration of a substance above which it is predicted that the general population, including susceptible individuals, could experience life-threatening adverse health effects or death.

ACGIH = American Conference of Governmental Industrial Hygienists;

AEGL = Acute Exposure Guideline Level;

CFR = Code of Federal Regulations;

EPA = Environmental Protection Agency;

IDLH = immediately dangerous to life or health;

NIOSH = National Institute for Occupational Safety and Health;

OSHA = Occupational Safety and Health Administration;

REL=Recommended Exposure Limit;

STEL = short-term exposure limit;

TLV = threshold limit values;

TWA = time-weighted average;

WHO = World Health Organization



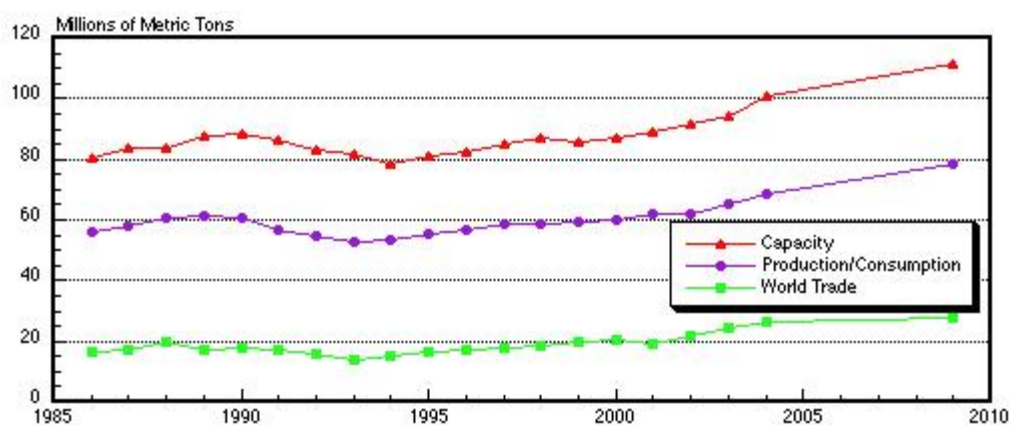


FIGURE 4: World supply/demand for sulphur in all forms  
(Suresh, 2006)

Fertilizers are the ultimate end use of about 50% of the world's sulphur production. Phosphate fertilizer production accounts for about 85% of this total, but ammonium sulphate production is also significant. Thus, the sulphur market is very dependent upon the cyclical world phosphate fertilizer market. Global phosphate fertilizer consumption spiked in 2004–2005. However, it is expected to grow at a nominal rate of about 1.9% from 2004 to 2009. Demands for downstream products like phosphoric acid-based superphosphate and potassium sulphate contribute to sulphur demand. There is no substitute for phosphates in their role as a plant nutrient (Suresh, 2006). Sulphur and sulphur-containing intermediate products are also used in the following industries: plastics and other synthetic products, paper products, paints, soil and water treatment, animal nutrition, highway construction, coatings, mortar substitute, foams, sulphur impregnation, petroleum refining, nonferrous metal production, iron and steel production, and other uses (Kirk-Othmer, 2006).

Based on reports emitted by the U.S. Geological Survey, the average price for elemental sulphur in the United States, during the period 2001–2006, was around 23.71 USD/ton.

## 4.2 Carbon dioxide

The carbon dioxide business is traditionally thought of as the recovery and distribution of liquid carbon dioxide. Liquid carbon dioxide is usually recovered as a gaseous by-product of industrial operations. The gaseous carbon dioxide is liquefied for sale as a merchant product because liquid carbon dioxide can be transported more economically than the gaseous form and because many consumers use carbon dioxide for the physical properties associated with its being as a refrigerated liquid. Liquid carbon dioxide reaches end users through a network of highway tankers, resupply depots and railcars. As a result, the carbon dioxide business is highly regional (Suresh, 2007).

### *Supply/demand*

Typical sources of carbon dioxide for commercial carbon dioxide recovery plants are (Pierantozzi, 2003):

- a) Synthetic ammonia and hydrogen plants in which methane or other hydrocarbons are converted to carbon dioxide and hydrogen;
- b) Flue gases resulting from the combustion of carbonaceous fuels;
- c) Fermentation in which a sugar such as dextrose is converted to ethyl alcohol and carbon dioxide;
- d) A lime-kiln operation in which carbonates are thermally decomposed;
- e) Sodium phosphate manufacture; and
- f) Natural carbon dioxide gas wells.

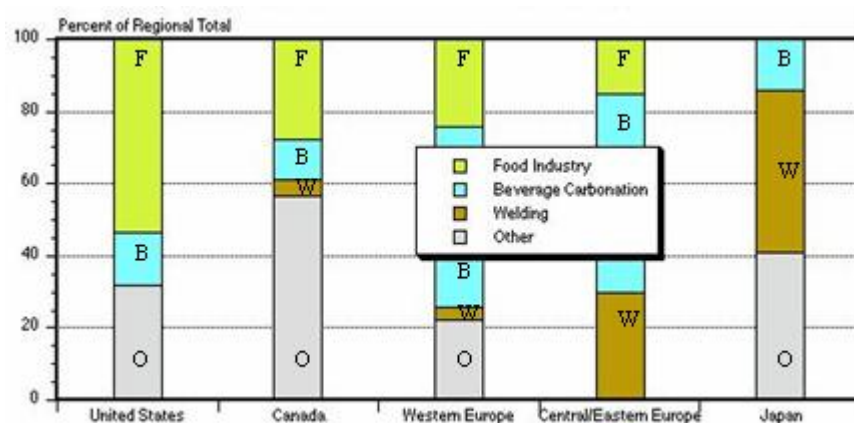


FIGURE 5: Consumption of carbon dioxide by end-use, 2006 (modified from Suresh, 2007)

Liquid carbon dioxide consumption is likely to grow at an average annual rate of about 1.6% in the United States, 4.4% in Western Europe and 1.0% in Japan over the next five years. China is continuing to emerge as an important player in the global market. For the past few years, the country's consumption has been growing at rates close to 15–20% annually and is expected to continue to

grow around that range in the forecast period. Capacity has almost quadrupled in the past decade since China opened its doors to Western enterprises. Figure 5 shows the consumption of carbon dioxide by end use for different regions (Suresh, 2007).

Carbon dioxide in the food industry is generally used for food freezing or chilling and is commonly purchased in liquid form but may be used in any form. Numerous patents on applications and equipment for these applications have been received. Carbon dioxide is also widely used for beverage carbonation; both soft drinks and beer production consume the largest quantity of CO<sub>2</sub>. Applications of solid carbon dioxide (dry ice) include refrigeration of foodstuffs, especially ice cream, meat products, and frozen foods. Dry ice is also used to chill aluminium rivets. These harden rapidly at room temperature, but remain soft if kept cold with dry ice. Dry ice has found numerous uses in laboratories, hospitals, and airplanes as a convenient and readily available low-temperature coolant.

Liquid carbon dioxide provides the most readily available method for rapid refrigeration and is used for rapid chilling of loaded trucks and rail cars before shipment. Fire-extinguishing equipment, ranging from hand-type extinguishers to permanent installations in warehouses, chemical plants, ships, and airplanes, uses liquid carbon dioxide. The addition of small amounts of carbon dioxide to the atmosphere in greenhouses greatly improves the growth rate of vegetables and flowers.

As a weak acid (in aqueous solution), carbon dioxide neutralizes excess caustics in textile manufacturing operations. Carbon dioxide is also used for neutralizing alkaline wastewaters, treating skins in tanning operations, and carbonating treated water to prevent scaling (Pierantozzi, 2003).

In El Salvador, the main use of CO<sub>2</sub> is for beverage carbonation, and it is mainly imported from Mexico. Since information about the price of liquid CO<sub>2</sub> in the Salvadorian market is not available, data from Iceland is used, where the price for liquid CO<sub>2</sub> in September 2007 was 25 ISK/kg, equivalent to 0.384 USD/kg.

#### 4.2.1 Carbon credits

The Kyoto Protocol's major feature is that it has mandatory targets on greenhouse gas emissions for those of the world's leading economies which have accepted it. These targets range from an 8% to 10% reduction of the countries' individual 1990 emissions levels, with a view to reducing their overall emissions of such gases by at least 5% below existing 1990 levels in the commitment period, 2008 to 2012. Future mandatory targets are expected to be established for "commitment periods" after 2012. These are to be negotiated well in advance of the periods concerned (UNFCCC, 2007).

Established in the Kyoto Protocol, the Clean Development Mechanism (CDM) provides for industrialized countries to implement project activities that reduce emissions in developing countries, in return for certified emission reductions (CERs). The CERs generated by such project activities can be used by industrialized countries to help meet their emissions targets under the Kyoto Protocol. To be certified by the Clean Development Mechanism Executive Board, a project must be approved by all involved parties, demonstrate a measurable and long-term ability to reduce emissions, and promise reductions that would be additional to any that would otherwise occur (UNFCCC, 2007).

A geothermal project that displaces a bunker-fired thermal plant will be allowed a number of CERs each year equivalent to what the thermal plant would have produced in that year. Each CER can then be sold in the international carbon market. Prices for CERs in the spot market can be very volatile, but contracts can be made to reduce volatility (Rodríguez and Herrera, 2007). Based on CER market reports published on the internet, CER prices ranged between 8 and 15 Euros/ton in August, 2007.

There are currently two geothermal projects in El Salvador that are certified to emit CERs: the 44 MW Berlín Third Unit and the 9.3 MW Berlín Binary Cycle.

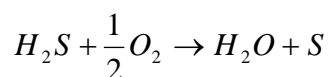
## 5. OVERVIEW OF METHODS FOR HYDROGEN SULFIDE REMOVAL

This section describes some existing methods used for H<sub>2</sub>S removal in different types of industries, such as gas, oil and also geothermal. The processes can be classified as liquid-redox and gas phase oxidation. A brief description of each process, the main steps and chemical reactions involved, applications, limitations and other issues are included.

### 5.1 Liquid-redox methods

Liquid-redox processes have been used in the gas industry for decades, and research has continuously been carried out in order to improve efficiency and reduce costs. Liquid-redox plants are believed to be practical for feeds of about 1-30 MMscfd of gas containing 0.05-5.0 mole % of H<sub>2</sub>S; they can be used for geothermal vent gas treatment and are able to handle fluctuating inlet gas flowrates and H<sub>2</sub>S concentration. Some geothermal power stations in the world, mostly in the U.S., have liquid-redox H<sub>2</sub>S abatement systems installed, including the LO-CAT and Stretford methods.

In the liquid-redox processes, the sour gas is contacted with an alkaline scrubbing solution to dissolve the H<sub>2</sub>S as HS<sup>-</sup>. The HS<sup>-</sup> is oxidized to elemental sulphur. The main difference in the liquid-redox methods is in the way oxidation is carried out. The overall chemical reaction in all the liquid-redox processes is:



#### 5.1.1 Stretford process

##### *Development and applications*

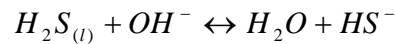
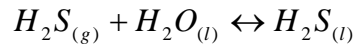
This is the first liquid-redox process, developed during the 1940s. In 1989 this was one of the major processes offered in the U.S marketplace and was installed in many plants for gas treatment from oil, gas and geothermal industries. However, since the 1990s the method has been selected by few new plants due to environmental concerns (Dalrymple and Trofe, 1994).

##### *Process description*

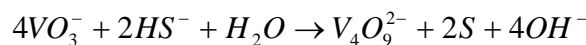
The method uses a scrubbing solution containing vanadium in the plus 5 valence state (V<sup>+5</sup>) and anthraquinone disulfonic acid (ADA) in a sodium carbonate solution. The Stretford process is based

on a series of liquid phase oxidation-reduction reactions. The following are the main steps of the process:

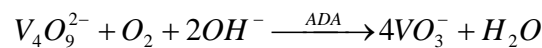
- a) The gas containing  $H_2S$  is brought into contact with the alkaline scrubbing solution and an acid/base reaction occurs:



- b) The resultant bisulphide ion ( $HS^-$ ) is oxidized by the  $V^{+5}$  to produce elemental sulphur;  $V^{+5}$  is reduced to  $V^{+4}$  and the hydroxyl ions are regenerated:



- c) The solution is routed to the oxidizer, where  $V^{+4}$  is regenerated back to  $V^{+5}$  and sulphur is removed by flotation. Oxidation of vanadium is done by oxygen in the presence of ADA:



- d) Sulphur is recovered by filters or centrifuges; sulphur cake may be disposed of as a solid waste or purified by autoclaving.

#### *Benefits and limitations*

- A lot of experience is gathered in its application.
- Elemental sulphur is formed as a by-product, which can be sold after purification.
- Sulphur salts may form rather than elemental sulphur and these salts must be disposed of.
- Possible plugging in equipment may occur during operation.
- The most significant problem associated with this method is the production of toxic wastes. Environmental concerns and the high cost of vanadium waste disposal are the main reasons for avoiding this method in new applications.

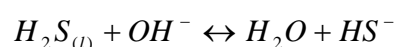
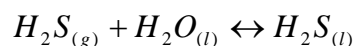
### **5.1.2 LO-CAT process**

#### *Development and applications*

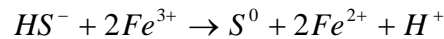
This method was commercialized in the late 1970s and has been applied to the treatment of natural gas, biogas, landfill gas and NCG from geothermal power plants (Matthíasdóttir, 2006). The company Gas Technology Products developed a process for special application in geothermal power plants, the LO-CAT II; this system is at present offered in the market.

#### *Process description*

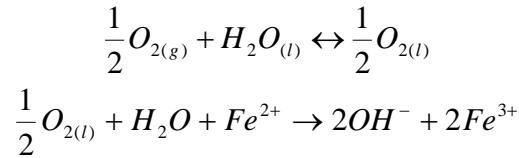
- a)  $H_2S$  is absorbed in an alkaline scrubbing solution and  $HS^-$  is formed, as in the Stretford process. The following chemical reactions occur:



- b)  $HS^-$  ion is oxidized to elemental sulphur by a ferric ion complex compound; an iron chelated solution is used. The chelating agent prevents the reaction between  $Fe^{3+}$  and the  $OH^-$  ions in the alkaline solution, avoiding the precipitation of  $Fe^{3+}$  as  $Fe(OH)_3$ ;  $Fe^{+3}$  is reduced to  $Fe^{+2}$ :



c)  $Fe^{+2}$  is oxidized to  $Fe^{+3}$  by using air:



d) Elemental sulphur is removed as slurry and filtered to obtain a 60-65% by weight sulphur cake.

A process flow diagram is shown in Figure 6.

#### Benefits and limitations

- 99.9% of  $H_2S$  removal efficiency can be achieved.
- Non-hazardous wastes are produced and purges can be recycled.
- Typically poor quality sulphur is recovered and has to be disposed of as a solid waste.
- Possible formation of thiosulfate and bicarbonate; the addition of a caustic may be required.
- Possible plugging in equipment during operation.
- At present, this method is used in geothermal power plants, for instance in Geysir Unit 15, U.S.A.

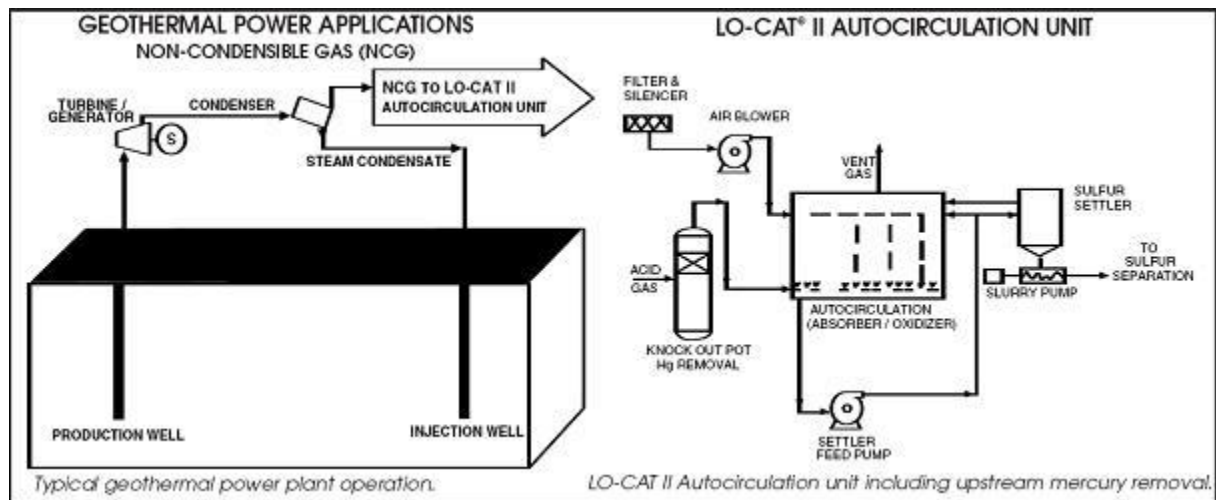


FIGURE 6: LO-CAT II process flow diagram (Gas Technology Products, 2007)

### 5.1.3 SulFerox process

#### Summary of the process

The same principle as in the LO-CAT method is used. The main differences are that the oxidation and regeneration steps are carried out in separate vessels; sulphur is recovered from the filters, melted and sent to sulphur storage; a higher concentration of iron chelates is used, which allows for lower circulation rates and smaller equipment sizes (Korens et al., 2002).

Usually, up to 99% of sulphur recovery can be achieved, however, poor quality sulphur is obtained.

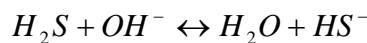
### 5.1.4 THIOPAQ process

#### *Development and applications*

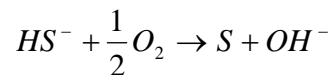
This process was developed by the Dutch company Paques B.V. in 1993 and later, together with Shell Global Solutions and UOP LLC, the process was improved and commercialized for applications in industries such as pulp and paper, chemical, and mining. THIOPAQ has been applied since 1993 for removing H<sub>2</sub>S from biogas and landfill gas, around 25 units are installed in Germany, U.K., Denmark, France, Spain, Italy, India, USA (Matthíasdóttir, 2006).

#### *Process description*

- a) The H<sub>2</sub>S containing gas is contacted with an alkaline solution at pH between 8 to 9, as in the other liquid-redox processes; HS<sup>-</sup> is formed:



- b) HS<sup>-</sup> is oxidized to elemental sulphur in a bioreactor by colorless sulphur bacteria (Thiobacillus). The hydroxide used in the scrubber is thus regenerated in this stage:



- c) The slurry can be dewatered by a decanter-centrifuge and then the sulphur cake can be dried to a 90% solid content or be purified further, by melting, to high quality sulphur.

A process flow diagram is shown in Figure 7.

#### *Benefits and limitations*

- 99.5% of H<sub>2</sub>S removal efficiency can be achieved.
- The biological sulphur cake produced can be used for agricultural purposes.
- Relatively little control is required.
- There is less chance of plugging compared with the Stretford and LO-CAT processes.
- This method has not been applied in geothermal power plants; pilot tests may, therefore, be considered.

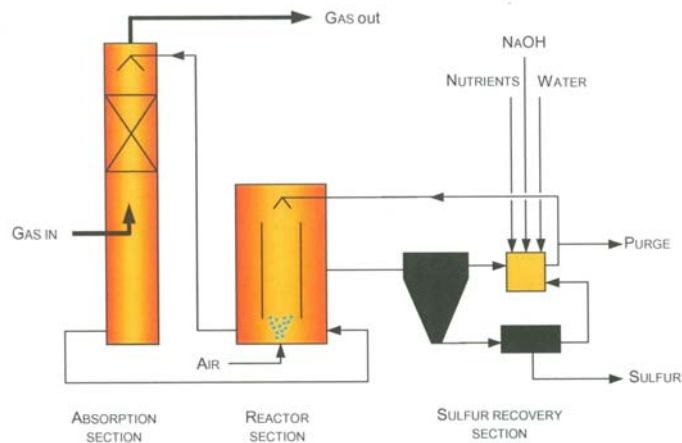


FIGURE 7: THIOPAQ process flow diagram

### 5.1.5 Fe-Cl Hybrid process

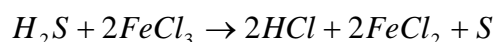
#### *Development and applications*

This technology was originally published by a group of Japanese scientists in 1991 and developed later by a group of Icelandic scientists for special application in geothermal power plants. There are no applications at present.

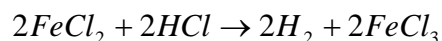
#### *Process description*

This process uses an acid FeCl<sub>3</sub> solution for chemical H<sub>2</sub>S absorption. Hydrogen is obtained by electrolysis, therefore electricity is needed in this stage; elemental sulphur is also obtained as a by-product.

- a) By absorbing in the highly acidic  $\text{FeCl}_3$  solution,  $\text{H}_2\text{S}$  is reduced and solid sulphur precipitates.  $\text{Fe}^{+3}$  ions are reduced to  $\text{Fe}^{+2}$ :



- b) Solid sulphur is filtered and removed from the solution.  
c) By electrolysis,  $\text{Fe}^{+2}$  is converted back to  $\text{Fe}^{+3}$  and hydrogen is produced:



### *Benefits and limitations*

- A previous study concluded that this method suits the conditions in the Nesjavellir power plant (the biggest geothermal power station in Iceland in 2007).
- The elemental sulphur obtained can be used as a fertilizer.
- Hydrogen (in high demand nowadays) can be used as a fuel.
- At present, this technology has a high cost and is underdeveloped. It has never been applied in any industry.
- Possible corrosion problems can be caused by the highly acidic solution used and also by sulphur in the electrodes (special care must be taken during material selection and in the sulphur filtering stage).

## **5.2 Gas phase methods**

These are also called dry-type methods, because the  $\text{H}_2\text{S}$  is oxidized in a gaseous phase, usually by using air and high temperature. The oldest and best known is the Claus process which has various modifications and extensions mainly applied to oil and gas industries. In recent years, new technologies using the gas phase oxidation principle have been developed and tested for geothermal applications.

### **5.2.1 Claus Process - Amine/Claus**

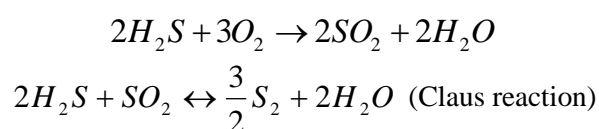
#### *Development and applications*

This process was developed by the chemist Carl Friedrich Claus in 1883. Applied in oil and natural gas industries, this is the standard process for removing sulphur from  $\text{H}_2\text{S}$  containing gases. Some modifications have been applied to the basic process in order to make it suitable for certain conditions in these industries.

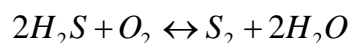
#### *Process description*

To the basic Claus process, one previous amine extraction stage has been added. The main steps are described below:

- Using amine extraction,  $\text{H}_2\text{S}$  is separated from the gas stream. The amine, with absorbed gases, is routed into a regenerator (a stripper with a reboiler), and the regenerated amine is recycled. The  $\text{H}_2\text{S}$ -rich stripped gas goes to the Claus process.
- $\text{H}_2\text{S}$  is partially oxidized with air at 1000-1400°C in a furnace. Elemental sulphur and  $\text{SO}_2$  are formed. This stage is the so-called thermal stage. The following reactions take place:



- c) By using catalytic converters in a series at temperatures of around 200-350°C and with an adequate H<sub>2</sub>S:SO<sub>2</sub> ratio, these components react and 95-97% of H<sub>2</sub>S can be converted. The overall reaction is:



- d) The gas coming from the catalytic reactor goes to a condenser, where gas is cooled to between 150-130°C.  
e) The liquid sulphur obtained is then collected.

#### *Benefits and limitations*

- Around 97% of the sulphur is recovered by using three stages.
- High heat is a requirement.
- There is no experience with this process in the geothermal industry.

### **5.2.2 Selectox process**

#### *Development and applications*

Licensed by U.O.P.Co, this method has two versions, the Straight Through Selectox and the Recycle Selectox; the latter is typically used for acid gas streams containing 5-40 mole% H<sub>2</sub>S. The Selectox process is based on replacing the Claus first stage thermal reactor (the furnace) with a catalytic oxidation step.

One H<sub>2</sub>S abatement system which combines the Selectox and Claus methods is in operation in one geothermal power plant in Japan (Yanaizu-Nishiyama). The system treats about 36 tons/h of NCG and 0.65 tons/h of H<sub>2</sub>S and works satisfactorily (Takahashi, 2000).

#### *Process description*

- a) H<sub>2</sub>S is oxidized and converted to SO<sub>2</sub> at a temperature of about 310°C; oxidation is caused using air with a catalyst such as aluminium oxide, based on silicon dioxide. The catalyst promotes the selective oxidation of H<sub>2</sub>S to SO<sub>2</sub>. This stage replaces the thermal stage in the Claus process and operates at a lower temperature.
- b) H<sub>2</sub>S reacts with SO<sub>2</sub> to form elemental sulphur; the process continues with the conventional Claus stages.

### **5.2.3 Wet gas sulphuric acid process (WSA)**

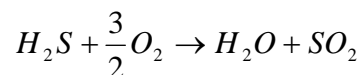
#### *Development and applications*

This was introduced by the Danish company Haldor Topsoe in the 1980s. It has been applied in oil refineries, petrochemical, cellulose, metallurgical, and mineral industries and in power plants (Matthíasdóttir, 2006).

#### *Process description*

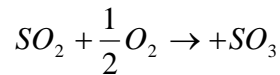
The principle is to convert H<sub>2</sub>S to commercial quality sulphuric acid. This process requires one catalyst based on a diatomaceous earth silica carrier impregnated with vanadium-pentoxide and sodium/potassium pyrosulphates to obtain the by-products: high quality sulphuric acid (97% by weight) and high pressure steam (12 bars, 350°C).

- a) H<sub>2</sub>S containing gas is incinerated to SO<sub>2</sub> in a burner:

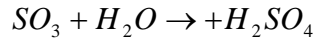


- b) SO<sub>2</sub> is converted to SO<sub>3</sub> in a catalytic reactor.





c)  $SO_3$  containing gas is cooled and reacts with water vapour to form gas phase sulphuric acid.



d) The gas phase sulphuric acid is condensated.

#### *Benefits and limitations*

- 95-99%  $H_2S$  removal efficiency can be achieved.
- Sulphuric acid can be sold.
- It has lower investment costs and better heat economy than the Claus process (Matthíasdóttir, 2006).
- High-pressure steam can be used for electricity production.
- Special care must be taken in material selection for the condenser, where sulphuric acid is produced.

### 5.2.4 XERGY process

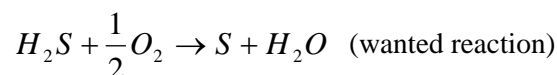
#### *Development and applications*

The Xergy ACT process (Advanced Catalytic Technology) was developed by Xergy Processing Inc. The first Xergy plant was installed in a petroleum application at a sour gas processing plant in Canada in 2003 (Monnery, 2005).

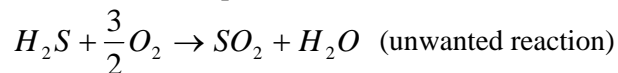
The XERGY process is applied for  $H_2S$  sulphur recovery in a sour gas stream, with production between 0.1 to 20 tons/day. There are two different versions of the process, the sub sulphur dew point and the above sulphur dew point. The first operates much the same as a sub dew point tail gas clean up or dry desiccant water/hydrocarbon dew point type process with a cyclic operation. The second operates like a converter in the modified Claus process, is simpler and less expensive but conversions are approximately 10% lower than for the sub dew point process.

#### *Process description*

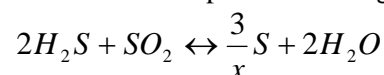
- a) The processed gas is heated to reaction temperature.
- b)  $H_2S$  is oxidized in a catalytic reactor by adding air. In the reactor, the oxidation of  $H_2S$  takes place according to:



An unwanted side reaction that can take place is the formation of  $SO_2$  according to:



In addition, the equilibrium Claus reaction takes place according to:



There is high selectivity of sulphur via the wanted reaction with appropriate control of the catalyst, temperature and oxygen.

- c) The sulphur formed is absorbed into the catalyst and later removed by adding heat to desorb and vaporize it (in the sub dew point process) or it stays in the vapour phase (in the above dew point process). In the sub dew point process, the reactor is switched to a regeneration cycle when it is full and the reactor that has been in a regeneration cycle is switched to a reaction cycle.
- d) Sulphur is recovered through condensation.
- e) The vapour is recycled back to the front end of the process.

A process flow diagram is shown in Figure 8.

#### *Benefits and limitations*

- Sulphur obtained as a by-product can be sold.
- There are no stream emissions.
- This process can be adapted to different H<sub>2</sub>S abatement requirements (“fit for purpose”).
- In his study, Monnery (2005) expressed that this method is ideally suited for H<sub>2</sub>S abatement in geothermal steam projects.

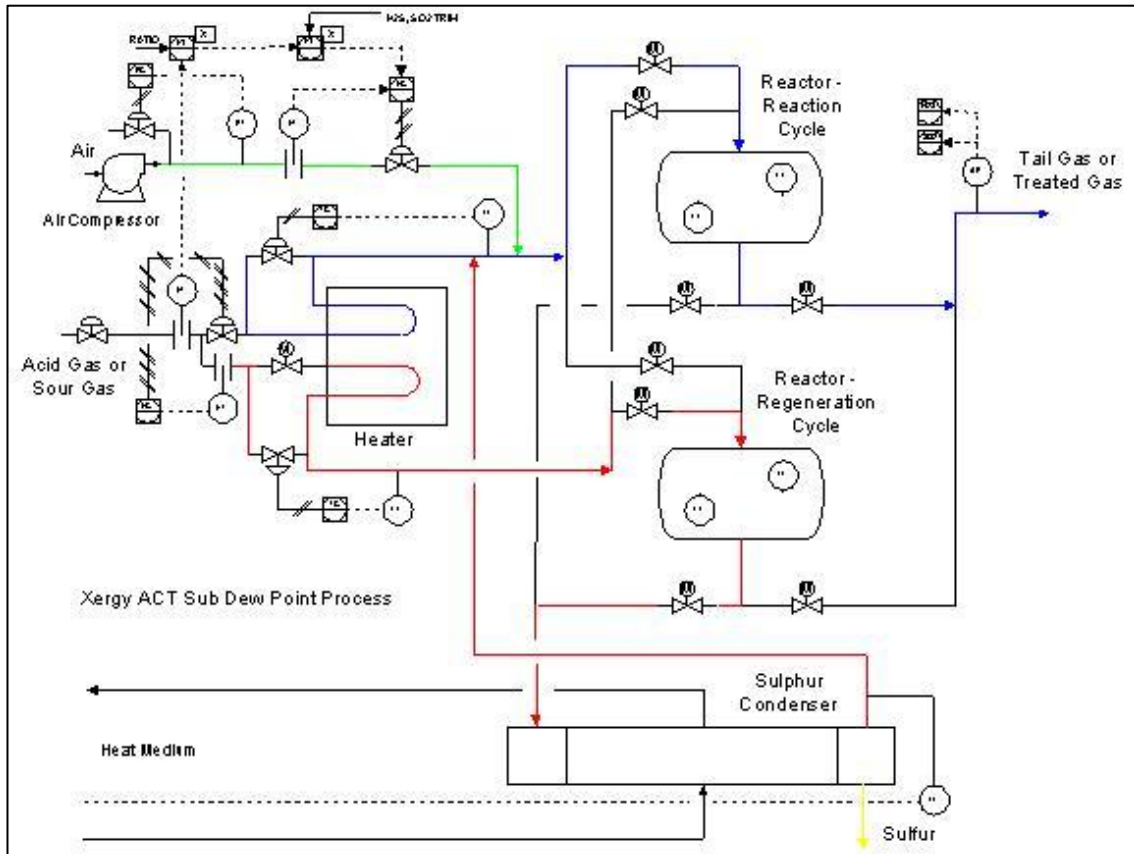


FIGURE 8: XERGY process flow diagram

### 5.2.5 AMIS process

#### *Development and applications*

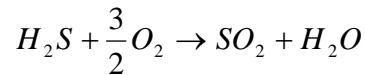
The AMIS method (Abatement of Mercury and Hydrogen Sulfide) was developed and patented by the Italian company ENEL Spa. and successfully applied for gas treatment in three existing geothermal power plants in Italy. The first AMIS plant started operation in February, 2002 and a second in July, 2003. About fifteen new AMIS plants were in design phase and expected to be put into operation in 2006 (Baldacci et al., 2005).

#### *Process description*

The process removes H<sub>2</sub>S and Hg from the gases extracted from the direct contact condenser in three main stages: removal of mercury by chemical absorption, selective catalytic oxidation of H<sub>2</sub>S, and SO<sub>2</sub> scrubbing by geothermal water.

- a) NCG leaving the condenser are cooled to about 70°C.
- b) Mercury is absorbed by selenium mass or sulfurized activated carbon (removal efficiency is higher than 95%).

- c) NCG are heated to around 240°C, the temperature suitable for H<sub>2</sub>S catalytic oxidation to SO<sub>2</sub>. Oxidation of H<sub>2</sub>S takes place by adding air (efficiency of conversion is 99% or more). This process is an exothermic reaction and the heat is recovered to heat up the NCG leaving the mercury removal stage:



- d) SO<sub>2</sub> is scrubbed in a packed column by using geothermal water (geothermal water means water flowing from the cooling tower), soluble sulphur compounds are formed such as sulphites, thiosulphites and thiosulphates. Adding sodium hydroxide or ammonia to the geothermal water can increase the SO<sub>2</sub> removal efficiency. The overflow of geothermal water goes to reinjection.
- e) Clean NCG are sent to the cooling tower for discharge to the atmosphere.

A process flow diagram is shown in Figure 9.

#### Benefits and limitations

- The method does not require the use of chemicals (if geothermal water contains enough ammonia) and does not produce sulphur-based by-products.
- There is no by-product to dispose of; reaction products are soluble and are reinjected with the overflow of the cooling tower.
- The overall reduction of plant emissions can total 95-99% for mercury and 75-85% for H<sub>2</sub>S.
- This technology has been applied in geothermal power plants with good results (Baldacci et al., 2005).

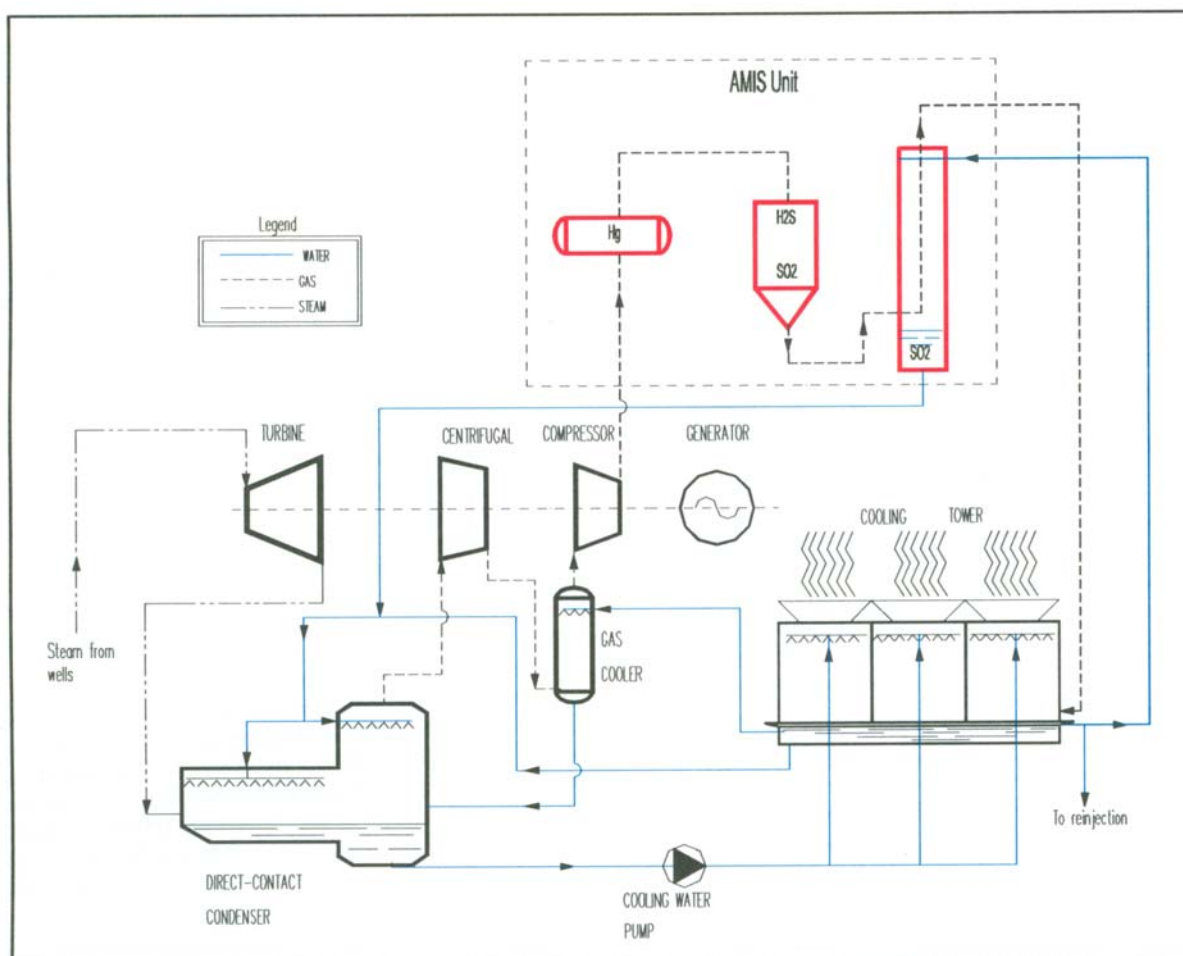


FIGURE 9: AMIS process flow diagram

### 5.3 Other methods for H<sub>2</sub>S removal

Gas injection is practiced in the natural gas and petroleum industries. There are many projects in operation in the United States and Canada. Since the emission regulations in these countries have become more stringent, and due to the high cost of sulphur recovery technologies and low sulphur prices, gas injection has been used as an economic way to reduce gas emissions, including H<sub>2</sub>S and CO<sub>2</sub> sequestration by default. There are three basic steps in the gas injection process: compression of the gases, pipeline and injection in a well. At present there is some controversy about disposing of gas in this way. It could lead to possible corrosion problems in pipelines. In a geothermal system, the effects on the reservoir are not known. It is also possible that injected gases will be re-extracted from the production wells.

One gas injection test through mixing with the separated brine was developed in the Philippines in 2001-2002, the Tongonan-1 CO<sub>2</sub> Gas Injection Project. The most significant results of the test were that gas injection is feasible only for partial reduction of gas emissions from geothermal power plants due to the large brine flow requirement. The investment cost could be 40-60% lower than other methods of gas abatement (LO-CAT). Decreasing the brine pH by using the acid gas did not cause corrosion problems and avoided calcite scaling. Although the method is simple, it may be difficult to operate and maintain (Villena et al., 2005).

There are other significant experiments for H<sub>2</sub>S removal from geothermal NCG. Hirowatari et al. (1995) reported the results of tests for H<sub>2</sub>SO<sub>4</sub> production from H<sub>2</sub>S in two geothermal power stations in Japan. The acid solution obtained could be used for scaling prevention by pH control in the brine. In those pilot scale experiments, H<sub>2</sub>SO<sub>4</sub> was produced by using three different methods including gas phase, biological and biochemical oxidation of H<sub>2</sub>S.

The first method tested was similar to the WSA method described above; the other two methods for H<sub>2</sub>SO<sub>4</sub> production have not been developed yet for industrial applications, according to Hirowatari.

The main conclusions were that these three methods for H<sub>2</sub>SO<sub>4</sub> production and scaling prevention could be suitable in the geothermal industry; however, none of them has been applied in a geothermal power station as efficiency needs to be improved (Hirowatari et al., 1995).

## 6. OVERVIEW OF METHODS FOR CARBON DIOXIDE TREATMENT

Reducing the amount of carbon dioxide emissions is imperative in order to curb global warming. Energy production using geothermal resources allows that; it is possible to reduce CO<sub>2</sub> emissions from geothermal resources. Carbon dioxide can be captured for reinjection in geothermal reservoirs or recovered as a by-product, and purified for different purposes.

### 6.1 Carbon sequestration in geological formations / geothermal reservoirs

Carbon sequestration can be defined as the process of capturing and securely storing carbon, which would otherwise be emitted to or remain in the atmosphere. Carbon sequestration can potentially become a major tool for reducing carbon emissions caused by the use of fossil fuels (Dastan et al., 2005); this technique can also be applied in the geothermal industry. Six technical and scientific areas have been established as the main process and methods defining CO<sub>2</sub> sequestration, before and after reaching the atmosphere; these are as follows:

- a) Separation and capture of CO<sub>2</sub>;
- b) Ocean sequestration;

- c) Carbon sequestration in terrestrial ecosystems;
- d) Advanced biological processes;
- e) Advanced chemical approaches;
- f) Sequestration of CO<sub>2</sub> in geological formations.

The most direct carbon management strategy for long-term removal of CO<sub>2</sub> from the atmosphere is CO<sub>2</sub> sequestration in geologic formations. This method is based on the principle that CO<sub>2</sub> injected into the geological formation is trapped, dissolved into the fluid phase and finally reacts with the minerals in the formation, becoming part of the solid mineral structure. In 2005, three industrial-scale carbon capture and storage projects were operating in the oil and gas industry in Norway, Canada and Algeria.

Meanwhile in the geothermal industry, the possibility of CO<sub>2</sub> sequestration has also been studied. In Ogachi geothermal reservoir, Japan, laboratory and field experiments were performed in order to study the CO<sub>2</sub>-water-rock interaction and prove the theory that CO<sub>2</sub> reacts with minerals in the geological formation upon which carbonates form. It is believed that CO<sub>2</sub> in a supercritical state can be injected into the reservoir at high temperatures and then be dissolved into the geothermal fluid, where the CO<sub>2</sub> saturated water would react with the surrounding rocks and form calcite and kaolinite by extracting Ca and Mg from the rocks. This theoretical process is shown in Figure 10. The results of the experiments suggest that CO<sub>2</sub> injected into geothermal fields can be fixed as carbonate minerals (Ueda et al., 2005).

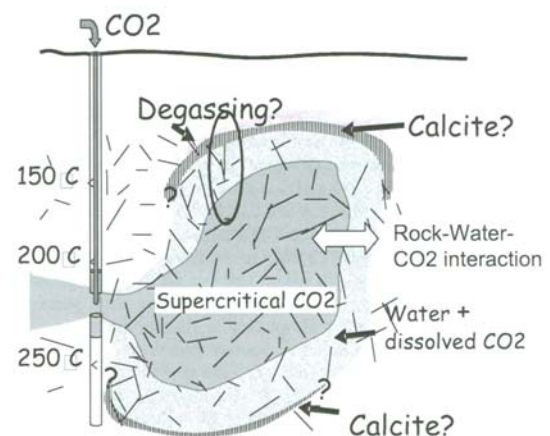


FIGURE 10: Theoretical behaviour of supercritical CO<sub>2</sub> injected in geothermal reservoir (Ueda, 2005)

Another study developed in the Kizildere high temperature geothermal field, Turkey, showed that it is possible to sequester very limited amounts of CO<sub>2</sub> for short periods of time, indicating that long term CO<sub>2</sub> sequestration is not feasible in high-temperature liquid-dominated highly fractured geothermal systems (Dastan et al., 2005).

In the Hellisheidi geothermal field, Iceland, a new research project for CO<sub>2</sub> storage was developed in 2007. The main goal of the project is to optimize industrial methods for storing CO<sub>2</sub> in basaltic rocks.

## 6.2 Carbon dioxide recovery

Carbon dioxide in geothermal NCG can also be recovered and used mainly in the food and chemical industry after purification and liquefaction or solidification (dry ice). In Kizildere geothermal field, Turkey, the CO<sub>2</sub> set free in the condenser is partly supplied to a liquefied CO<sub>2</sub> and dry ice factory installed next to the plant; about 120,000 tons/year of dry ice and liquefied CO<sub>2</sub> have been produced for the beverage industry (Mertoglu, 2005).

In Iceland, food grade carbon dioxide is produced from CO<sub>2</sub> gas coming from a borehole located in a low-temperature geothermal field. The CO<sub>2</sub> gas contains small quantities of H<sub>2</sub>S, which are removed in a purification process. In order to obtain clean CO<sub>2</sub> from geothermal NCG, the application of one of the methods of H<sub>2</sub>S removal described in Section 5 is required, followed by final purification.

The composition of the gas from the Berlín power plant after H<sub>2</sub>S removal (assuming an efficiency of 99%) is shown in Table 5.

TABLE 5: Estimated gas composition from Berlín geothermal power plant after H<sub>2</sub>S removal

Component	(%wt)
CO <sub>2</sub>	98.8
H <sub>2</sub> S	0.086
N <sub>2</sub>	1.07
H <sub>2</sub>	0.028
O <sub>2</sub>	0.015
Ar	0.012
CH <sub>4</sub>	0.0055
Total	100.01

### 6.2.1 Purification

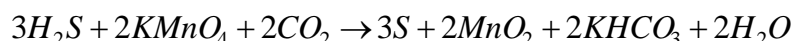
There is no standard process plant design for the recovery and purification of CO<sub>2</sub>. It depends on the source and the specific impurities present in the gas; however, a typical CO<sub>2</sub> purification plant includes the following unit operations:

- a) Compression; which allows the liquefaction of some condensable gases mixed with the CO<sub>2</sub>;
- b) Phases separation: Differentiated by their densities, liquid and gas phases are separated;
- c) Scrubbing; some water soluble compounds are removed from the gas usually by using a water/potassium permanganate system;
- d) Filtration (by absorption/adsorption): adsorbents such as carbon activated or absorbent compounds are used to remove a variety of inorganic impurities;
- e) Dehumidification: by using desiccant material, the moisture content of the gas is reduced;
- f) Condensation: a refrigerant is used to cool and condense the gas. Liquid carbon dioxide is obtained as a product.

The most commonly used purification methods are treatments with potassium permanganate, potassium dichromate, or active carbon. Companies around the world offer CO<sub>2</sub> purification plants based on flow and gas composition.

#### *Potassium permanganate.*

Probably the most widely used process for removing traces of hydrogen sulphide from carbon dioxide is to scrub the gas with an aqueous solution saturated with potassium permanganate. Sodium carbonate is added to the solution as a buffer. The reaction shown below takes place:



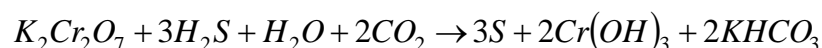
The precipitated manganese dioxide and sulphur are discarded. The solution is used until it becomes spent or so low in potassium permanganate that it is no longer effective; it is then discarded and replaced.

It is customary to place two scrubbers in a series, with the liquid flow countercurrent to the gas flow, to more efficiently use the permanganate solution. When the solution in the first scrubber is spent, with respect to the gas, the positions of the scrubbers are reversed and the spent scrubber is recharged with a fresh solution.

Two types of scrubbers are used. The simpler consists of a vessel half or two-thirds full of solution. The gas feeds into the bottom of the vessel and bubbles up through the solution. The other scrubber is a small packed tower through which the gas stream is passed countercurrent to a recirculating shower of potassium permanganate and soda ash solution. The latter requires a circulating pump and a solution mix chamber, but has the advantage of reducing the pressure drop through the equipment to a minimum. The solution is used until spent and then discarded. Two scrubbers of this type may also be used to improve efficiency (Pierantozzi, 2003).

#### *Potassium dichromate.*

This method is similar in application to the potassium permanganate method:



The precipitated chromic hydroxide and sulphur are discarded. This process is mainly used to purify carbon dioxide from fermentation (Pierantozzi, 2003).

#### *Active carbon.*

This process is also mainly used for purification of carbon dioxide from fermentation. These gases may contain impurities such as aldehydes, acids, higher alcohols, glycerol, furfural, glycol and hydrogen sulphide.

Carbon dioxide gases are collected in a low-pressure gas holder to even out the flow. Blowers force the gases through scrubbers where they are washed with water to remove the bulk of entrained material, alcohols, aldehydes, etc. The washed gases pass through active-carbon purifiers, which adsorb the balance of impurities, and proceed to the compressors. The adsorption process gives off heat, which is removed by water coils embedded in the carbon. Periodically, the carbon beds must be reactivated to remove accumulated impurities. This is accomplished by passing live steam through the carbon bed and water coils. After steaming, the carbon beds are dried by passing air through them; they are then ready for reuse. In general, two sets of active-carbon purifiers are used, one on-stream and the other being reactivated (Pierantozzi, 2003).

### **6.2.3 Liquefaction and solidification**

#### *Liquid CO<sub>2</sub> as a product*

Carbon dioxide may be liquefied at any temperature between its triple point (216.6 K) and its critical point (304 K) by compressing it to the corresponding liquefaction pressure, and removing the heat of condensation. There are two liquefaction processes. In the first, the carbon dioxide is liquefied near the critical temperature; water is used for cooling. This process requires compression of the carbon dioxide gas to pressures of about 7600 kPa (75 atm.). The gas from the final compression stage is cooled to about 305 K and then filtered to remove water and entrained lubricating oil. The filtered carbon dioxide gas is then liquefied in a water-cooled condenser.

The second liquefaction process is carried out at temperatures between 261 and 296 K, with liquefaction pressures of about 1600-2400 kPa (16-24 atm.). The compressed gas is pre-cooled to 277 to 300 K, water and entrained oil are separated, and the gas is then dehydrated in an activated alumina, bauxite, or silica gel drier, and flows to a refrigerant-cooled condenser. The liquid is then distilled in a stripper column to remove non-combustible impurities. Liquid carbon dioxide is stored and transported at ambient temperature; larger quantities are stored in refrigerated insulated tanks maintained at 255 K and 2070 kPa (20 atm.), and transported in insulated tank trucks.

#### *Solid CO<sub>2</sub> as a product*

Liquid carbon dioxide from a cylinder may be converted to "snow" by allowing the liquid to expand to atmospheric pressure. This simple process is used only where very small amounts of solid carbon dioxide are required because less than one-half of the liquid is recovered as a solid.

Liquid carbon dioxide from a supply tank at 700 kPa (7 atm.) and 227 K is fed to the press chamber through an automatic feed valve. The pressure in the press is maintained slightly above the triple point (480-550 kPa). The quantity fed to the press may be controlled by a timer, or a device that measures the liquid level in the press chamber. The pressure is reduced and the evolved CO<sub>2</sub> vapour is returned to a recycle system. When the pressure falls below the triple point (518 kPa), the liquid CO<sub>2</sub> solidifies to form carbon dioxide snow. Heat-exchange units are used to cool the liquid CO<sub>2</sub> with cold vapours from the press. About 50% of the liquid fed to the press remains as snow when the pressure has dropped close to atmospheric pressure. The hydraulic rams then press the snow into a solid block of dry ice. The block moves along a conveyor belt and is cut by band saws into four blocks, which are subsequently carried through automatic weighing and packaging machines. Carbon dioxide is ordinarily dehydrated during the liquefaction cycle to prevent freeze-ups in the condenser and flow valves in the liquid lines (Pierantozzi, 2003).

## 7. EVALUATION OF PROCESSES FOR GAS EMISSION ABATEMENT

Some of the methods for H<sub>2</sub>S removal offer advantages or aspects more desirable than others. The Stretford method can be discarded as a real option due to environmental problems related to the use of vanadium. New technologies such as THIOPAQ, AMIS and XERGY can most likely be successfully applied in geothermal power plants. Sulphuric acid production by WSA, and biological and biochemical processes encourage making deeper analyses and new tests for individual cases in different geothermal power plants, since the by-product acid obtained can be used for the prevention of scaling. Carbon dioxide recovery can be an attractive business due to the good prices paid for the liquid carbon dioxide in the local markets. Methods for CO<sub>2</sub> sequestration have not been well studied to date.

In order to make a preliminary feasibility analysis for the application of an H<sub>2</sub>S removal and CO<sub>2</sub> recovery method in the Berlín power plant, an economical assessment was carried out (see Section 7.1). The THIOPAQ method was chosen for this study, mainly because cost data for Icelandic conditions are available for this process. The evaluated CO<sub>2</sub> cleaning method was also chosen because of available data. The chosen methods may, therefore, not be the most economical; however, the results of the evaluation should give an indication of whether or not it is justified to make a more complete analysis for the application of other methods.

### 7.1 Economical assessment

The methodology for the cost estimation is described in: *Plant design and economics for chemical engineers* (Peters et al., 2003). The accuracy of the estimate is  $\pm 30\%$ , but should nevertheless be sufficiently accurate to provide a reliable decision. Fixed-capital investment (F.C.I.), production costs and revenue, from the sale of the by-product produced by the method applied, are calculated. The components used for the estimations are shown in Tables 6 to 9.

Budgetary quote information presented by companies offering gas treatment technologies for Icelandic geothermal power plants will be used for estimating the F.C.I. and operational costs for the Berlín power plant by scaling up/down, considering the capacities of the plant and updating the costs by using the chemical engineering cost index at each point.

The following equations were used for scaling and updating costs:

Purchase equipment costs:

$$\text{Cost of Berlín} = \text{Cost of Nesjavellir} \left( \frac{\text{Capacity of Berlín}}{\text{Capacity of Nesjavellir}} \right)^{0.6}$$

Utilities costs:

$$\text{Cost of Berlín} = \text{Cost of Nesjavellir} \left( \frac{\text{Capacity of Berlín}}{\text{Capacity of Nesjavellir}} \right)$$

Civil works costs:

$$\text{Cost of Berlín} = \text{Cost of civil works in E.S.} \left( \frac{\text{Area of Berlín}}{\text{Area of civil works in E.S.}} \right)$$

Considering that most of the equipment has round shape:

$$\text{Area of Berlín} = \text{Area of Svartsengi} \left( \sqrt{\frac{\text{Capacity of Berlín}}{\text{Capacity of Svartsengi}}} \right)$$



$$\text{Present cost} = \text{Original cost} \left( \frac{\text{Index value at present}}{\text{Index value at time original cost was obtained}} \right)$$

Some considerations taken into account in the cost estimation are:

- Excess water from the condenser can be used as cooling water; therefore, the cost for this utility is not taken into account.
- Costs for land acquisition and service facilities are not included in the estimation because they are already available in the existing plant; costs for transportation and storage of CO<sub>2</sub> in the client place are not considered.
- Some facilities required in the gas treatment processes are already in the geothermal plant.
- One person each is needed for operation and supervision for each process.
- The total F.C.I. cost will be financed with a 6 year payback period bank loan; the loan is a constant periodic payment for the fixed period.

TABLE 6: Individual components of the total fixed-capital investment cost

Fixed-capital investment	Value
<i>Direct cost</i>	
Purchased equipment (P.E.)	Budget quotation
Installation of purchased equipment	25% of P.E.
Instrumentation and controls	26% of P.E.
Piping (installed)	40% of P.E.
Electrical systems (installed)	20% of P.E.
Buildings (including services), yard improvements, service facilities (installed), land	Estimated for civil works in El Salvador
<i>Indirect cost</i>	
Engineering and supervision, construction expenses, legal expenses, contractor's fee, contingency	Budget quotation – Estimated for El Salvador

TABLE 7: Individual components of the total production costs

Production cost	Value
<i>Manufacturing cost</i>	
<i>Variable cost</i>	
Raw materials	Specific for each process
Utilities	
Catalyst	
Maintenance and repair	7% of P.E.
Operating labor and supervision	Estimated for El Salvador
<i>Fixed charges</i>	
Finance	Estimated for El Salvador
Local taxes, insurance	4% of F.C.I.
Plant overhead cost	60% of operating labour, supervision and maintenance costs
<i>General expenses</i>	
Administrative cost	15% of operating labour cost

#### *Hydrogen sulphide removal*

In 2005, PAQUES presented to the Technological Institute of Iceland a  $\pm 25\%$  cost estimate for capital expenditures (F.O.B.) and operational cost for the THIOPAQ H<sub>2</sub>S removal process applied to the Nesjavellir power plant. By using this budgetary quote and the information contained in Tables 6-9, cost estimations for the application of this process in the Berlín power plant have been made. The results are shown in Table 10.

TABLE 8: Cost data for utilities and by-product prices

Utilities	Cost	By-product	Prices
Electricity	0.09 USD/kWh	Sulphur	26 USD/ton
Cooling water	0	Liquid CO <sub>2</sub>	500 USD/ton
Demineralized water	0.3 USD/m <sup>3</sup>	CER	15.71 USD/ton

TABLE 9: Currency values and chemical engineering plant cost indices

Loan	Value	Currency	Cost index	Year
Payback period	10 years	1 Euro = 1.955 DEM (Jan 2000)	394.1	2000
Months per year	12 (equal)	1 Euro = 0.950 USD (June 2000)	468.4	2005
Nominal interest rate	7.0%	1 Euro = 1.186 USD (December, 2005)	530	April, 2007

TABLE 10: Cost estimate for the THIOPAQ H<sub>2</sub>S removal process

Costs / Revenue	Amount Nesjavellir (Units)	Cost Nesjavellir (Euro)	Amount Berlín (Units)	Cost Berlín, in 2007 (USD)
<b>Capital investment</b>				
Purchased equipment and installation		3,500,000		2,827,120
Instrumentation and controls			26% P.E.	588,041
Piping (installed)			40% P.E.	904,679
Electrical systems (installed)			20% P.E.	452,339
Engineering and supervision		75,000		60,581
License and know-how fee		400,000		230,334
Buildings (including services), yard improvements, service facilities (installed), contingency			200 m <sup>2</sup> (outdoor)	506,953
<b>Fixed-capital investment</b>				<b>5,570,047</b>
<b>Product cost</b>				
Electricity	319 (kW)		136.88	107,917
Maintenance and repairs			7% of P.E.	158,319
Catalyst: Nutrients for bacteria	390,000 (USD/year)		167,347 (USD/year)	189,355
Operating labour and supervision			2 people	21,600
Local taxes, insurance			4% of F.C.I.	222,802
Plant overhead			60% op., sup., maint. costs	107,951
Administrative expenses			15% op., sup., costs	3,240
<b>Total product cost</b>				<b>811,185</b>
Loan for F.C.I..				5,570,047
Interest			7.0%	
Repayment period			6 years	
Annual payment				1,168,573
<b>Total annual cost</b>				<b>1,979,757</b>
<b>Revenue</b>				
Sulphur			2,565 tons/year	66,682
<b>Total annual revenue</b>				<b>66,682</b>

*Carbon dioxide cleaning*

As was made for the H<sub>2</sub>S removal process, the cost estimation for the CO<sub>2</sub> cleaning process was carried out using the information included in a budgetary quote presented in 2000 by a technological supplier for CO<sub>2</sub> purification and liquefaction to the Technological Institute of Iceland for application in the Svartsengi power plant. Considering that H<sub>2</sub>S removal must be made before CO<sub>2</sub> cleaning, the net expenses for H<sub>2</sub>S removal are regarded as raw material cost for the CO<sub>2</sub> purification process. Table 11 contains the results of the cost estimation.

TABLE 11: Cost estimate for the CO<sub>2</sub> cleaning process

Costs / Revenue	Amount Svartsengi (Units)	Cost Svartsengi (Euros)	Amount Berlín (Units)	Cost Berlín, in 2007 (USD)
<b>Capital investment</b>				
Purchased equipment, instrumentation and controls, piping, electrical systems, engineering and supervision, license and know-how fee		664,679		1,582,360
Installation			20% P.E.	316,472
Buildings (including services), yard improvements, service facilities (installed), contingency				279,504
<b>Fixed-capital investment</b>				<b>2,178,336</b>
<b>Product cost</b>				
Raw material			73.58	1,913,075
Electricity	200 (kWh/ton CO <sub>2</sub> )		200 (kWh/tons CO <sub>2</sub> )	468,000
Maintenance and repairs	7% of P.E.		7% of P.E.	46,434
Demineralised water	2 (m <sup>3</sup> /ton CO <sub>2</sub> )		2 (m <sup>3</sup> /tons CO <sub>2</sub> )	15,600
Operating labour and supervision			2 people	21,600
Local taxes, insurance			4% of F.C.I.	87,133
Plant overhead			60% op., sup., maint. costs	40,821
Administrative expenses			15% op., sup., costs	3,240
<b>Total product cost</b>				<b>2,595,903</b>
Loan for F.C.I.				2,178,336
Interest			7.0%	
Repayment period			6 years	
Annual payment				457,006
<b>Total annual cost</b>				<b>3,052,909</b>
<b>Revenue</b>				
CO <sub>2</sub> liquid			24,700 tons/year	9,484,800
CER			26,000 tons/year	408,460
<b>Total annual revenue</b>				<b>9,893,260</b>

According to Table 10, the cost of removing 2725 tons of H<sub>2</sub>S/year from the NCG in the Berlín power plant is about 1.98 million USD, or about 726 USD/ton H<sub>2</sub>S. On the other side, the income of about 0.6 million USD/year can be obtained by selling elemental sulphur.

If a CO<sub>2</sub> cleaning process is applied after removing the H<sub>2</sub>S, the total annual cost of producing 24,700 tons of food grade liquid CO<sub>2</sub> is about 3.05 million USD, or 124 USD/ton CO<sub>2</sub>, which is expected to be much lower than the price of liquid CO<sub>2</sub> in El Salvador. An annual income of about 9.4 million USD can be generated by selling food grade CO<sub>2</sub>, assuming a price of 0,384 USD/kg for food grade CO<sub>2</sub>.

The high cost of H<sub>2</sub>S removal can, therefore, most likely be recovered by cleaning the CO<sub>2</sub> from the NCG in the Berlín power plant to food grade CO<sub>2</sub> and selling it in El Salvador.

## 8. CONCLUSIONS AND RECOMMENDATIONS

Geothermal energy production should be increased in El Salvador. It is an environmentally friendly and indigenous resource which could help reduce petroleum dependence. Research for the application of new technologies should be carried out in order to enhance the advantages of geothermal energy.

Being the main compounds in the non-condensable gases emitted from the Berlín geothermal power plant, carbon dioxide and hydrogen sulphide can be successfully treated for elemental sulphur recovery and purified liquid carbon dioxide production. Environmental and economic benefits can be achieved: global warming and acidification of rain and soil would be reduced even more by using geothermal non-condensable gases, instead of releasing them to the atmosphere. Thus, attractive incomes can be generated by selling liquid CO<sub>2</sub> and carbon certified emission reduction credits.

Different methods for gas treatment could be applied in the Berlín power plant or in new geothermal plants to be constructed in El Salvador in the near future. The THIOPAQ process may not be the most economical method for H<sub>2</sub>S removal; therefore, other technologies should be economically evaluated.

A further study of the by-products market should be carried out, as well as an economic assessment for hydrogen sulphide removal and carbon dioxide cleaning processes by using budgetary quote information presented by companies offering technologies applicable in Salvadorian geothermal power plants.

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