H_2S ABATEMENT IN GEOTHERMAL PLANTS - EVALUATION OF PROCESS ALTERNATIVES

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ABSTRACT

A recently completed literature review shows that there is a plethora of methods currently available for H_2S abatement which may be adapted to geothermal installations. The work reported here is addressed to the problem of obtaining a preliminary assessment of various process options in order to identify the most modem, economically attractive and commercially significant ones. A short description of each method and comments on their performance are included. A preliminary evaluation is carried out, on the basis of a set of qualitative criteria, leading to a relatively small number of qualified processes. This selection facilitates the risk of rigorously searching for the optimum process(es), for given geothermal field conditions.

I. INTRODUCTION

Large scale exploitation of high-enthalpy geothermal fields necessitates application of an appropriate method for the abatement of H_2S, which is encountered in relatively small concentrations in the raw steam. The plethora of methods currently available for H_2S abatement, combined with the variability of geothermal resources (fluid composition, pressure, temperature, throughput, etc.) tend to create a rather large number of process alternatives. Careful assessment of such alternatives is necessary for the ultimate selection of the most appropriate method for a particular application.

The present work is addressed to the problem of obtaining a preliminary assessment of various process options. In particular, a methodology for screening various processes is described, based on a set of qualitative criteria. Additionally, information is provided for the most modern and commercially significant processes, including a short description of each method and comments on future trends. By using this evaluation methodology some processes or combination of processes are selected. Design considerations and use of economic criteria can further minimize the number of selected methods.

2. GENERAL CLASSIFICATION OF H_2S ABATEMENT METHODS

The classification of various H_2S abatement methods is based on the particular stream [or *point]* in the geothermal plant where each method can be applied. It is thus necessary to identify the possible release points of H_2S emissions to the atmosphere, in a typical geothermal power plant. This type of classification is already discussed in the Literature [Otte, 1989; Owen, 1984 ; Stephens *et al.*, 1980). In Table 1 there is a brief description of the release points in geothermal power plants.

Figure 1 is a simplified flow diagram of a typical geothermal power plant, depicting essentially all alternatives for H_2S abatement. There are three upstream abatement methods, where removal of H_2S takes place from the geothermal steam (A methods), five methods for removing H_2S from off-gas ejector stream (B methods), two methods which can remove H_2S dissolved in the condensate-cooling water mixture (C methods), and two hybrid systems treating both ejector off-gases and dissolved H_2S (D methods).

Table 1. Possible H_2S release points in geothermal facilities

- *Pre-energy conversion H_2S emissions*, e.g. releases during well drilling and well testing activities, pipeline venting and steam stacking.
- H_2S emissions in the noncondensable gas vent *downstream of the steam turbine*.
- *Cooling tower emissions.* Once the condensate reaches the cooling tower, the cascading action of the condensate and the induced draft in the tower strips most of the H_2S out of the water which is then emitted to the atmosphere with the cooling tower plume.

3. PROCESS EVALUATION

A preliminary assessment of H_2S abatement processes can be made and is briefly described here. It includes the following four steps:

3.1 Initial selection of candidate methods

The initial selection of processes from the literature, includes conventional abatement systems applied commercially, or innovative technologies that are favored for adoption to geothermal installations of commercial scale.

3.2 Classification of abatement methods into general categories

A description of this step is presented above (Table 1 and Fig. 1).

3.3 Preliminary assessment of individual processes

The following main qualitative criteria can be used for a preliminary assessment of the selected methods:

a. Condenser design

The compatibility of each method is examined with the two condenser types (*direct contact* and *surface condensers*) which are used in geothermal power plants. Each condenser type has some important features influencing operation of the geothermal unit.

important features influencing operation of the geothermal unit. For instance, direct contact condensers require smaller capital investment, compared with surface condensers, are easier to maintain and simpler to operate. Surface condensers favor the presence of H_2S in the condenser vent gases, while in the case of direct contact condensers, considerable amount of H_2S is dissolved in the condensate. An examination of the technical characteristics of each method shows that some of them are compatible with both types, while the rest are compatible with only one of them.

b. Efficiency of the abatement system

The efficiency of the selected methods is expressed as a percentage reduction of the total amount of H_2S entering the plant. A typical rule would require at least Y0% reduction of entering H_2S, or an upper limit of emissions based on the size of the plant (e.g. the allowable limit could be expressed as 0.2 Kg H_2S/MWh).

c. Composition of the geothermal fluid

The composition of the geothermal fluid is very critical to process selection. The amount of H_2S dissolving in either the circulating water (direct contact condenser) or steam condensate (surface condenser) depends on the chemical composition of the steam. Of particular significance are the acidic and basic gases (CO_2, $B(OH)_3$, SO_2, H_2S, and NH_3). Additionally, the total amount of gas present must be known. This may be due to air leakage, non-condensable gases in the geothermal fluid and, in the case of direct contact condenser designs, air dissolved in the circulating water. A key point in geothermal design is that, over the lifetime of the project, wells will vary in their composition and for any process to be successful it must be sufficiently flexible to accommodate such changing conditions.

d. Process economics

The abatement methods can be categorized in four groups based on capital investment and operating costs:

(i) Low capital and operating costs
(ii) High capital and low operating costs
(iii) Low capital and high operating costs
(iv) High capital and operating costs

The most common cases are (ii) and (iii). Obviously case (i) is the most favorable, while case (iv) is the least desirable. Generally, methods of case (ii) are more suitable for big units with an extended operating period. On the contrary, methods of case (iii) are suitable for smaller units of relatively short life.

e. Other factors

Several factors influencing the selection of an abatement system can be recognized:

- Process flexibility
- Environmental impact
- Health and safety
- Corrosion problems
- Other unique operating advantages or disadvantages related with individual processes

3.4 Final selection of candidate methods

By using the above criteria, the number of candidate methods can be significantly reduced. Design considerations and use of economic criteria can further reduce the number of qualified processes.

4. REVIEW OF THE MAJOR H_2S ABATEMENT METHODS

In the following, the major H_2S abatement processes with known commercial use are grouped and presented according to the aforementioned general categories. There are comments outlining first the main characteristics of each category. For each method there is a brief process description, and the most important advantages and disadvantages are summarized. Methods are identified by symbols as shown in Fig. 1 (e.g. A1, B2, etc.).

Upstream Abatement Methods (A Methods).

In this category there are two H_2S abatement alternatives:

- Direct treatment of the total amount of geothermal steam to remove H_2S

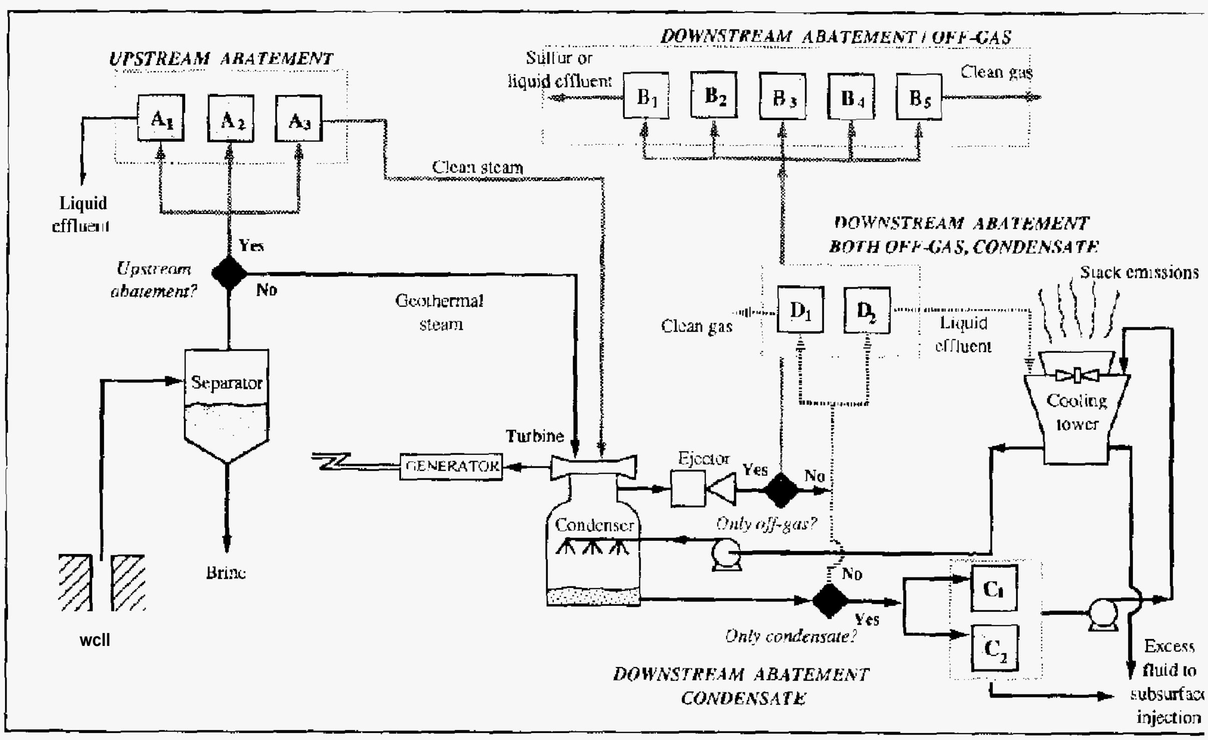

Fig. 1 Various options for hydrogen sulfide abatement in a power plant using geothermal steam

- Separation of the noncondensable campounds from geothermal steam and further treatment of noncondensables with an appropriate process

The main advantages of the processes in this category are the following:

- Protection of turbine components from corrosion, erosion and scaling.
- H_2S emissions control during steam stacking operations.
- In pre-energy conversion removal of H_2S, advantage is taken of the benefits associated with the use of a direct contact candenser (e.g. lower investment, easier maintenance, simple operation).
- Abatement is facilitated by treating a single stream only.
- A reduction of noncondensables entering the turbine condenser, leads to back pressure reduction and to improved efficiency of power production.
- With noncondensables removed from the vacuum system (ejectors), the steam requirements to achieve a certain vacuum are greatly reduced.

The main disadvantage of these processes appears to be thermal energy loss during sream treatment.

Downstream Methods. Off-gas Treatment (E Methods!

Methods of this category are capable of removing H_2S froin off-gas ejector streams (primary abatement) The majority are chemical processes, producing elemental sulphur from H_2S. all of them require a surface condenser which favors concentration of H_2S in the condenser vent gases. Methods of this category become Less effective in cases of high NH_3 concentration in geothermal steam. Ammonia promotes dissolution of considerable amounts of H_2S in the condensate and has a negative effect on H_2S removal efficiency.

Downstream Methods. Condensate Treatment (C Methods)

The processes of this category are capable of removing H_2S from the condensate produced in the condenser (secondary abatement) The major feature of these methods is that they are incapable of total H_2S removal.

Downstream Abatement. Hybrid Systems (D Methods)

The methods of this category have been developed recently. *They* can perform borh primary and secondary abatement, treating ejector off gases and condensate.

4.1 Copper sulfate nr EIC or Cuprosul Process (A1)

The proccss involves pre-energy conversion scrubbing of geothermal steam using an ammonium sulfate buffered acidic solution of copper sulfate. H_2S is converted to an insoluble copper sulfide precipitate which is subsequently recovered and fed to a copper sulfate regeneration process. The method is old with limited applications, involving relatively high operating expenses and significant capital investment (Owen and Michels, 1984; Stephens *et al.*, 1980; Coury and Vorum, 1977).

4.2 Scrubbing with alkali (A2 or B2)

The process can be used either upstream or downstream of the steam turbine and involves scrubbing of geothermal steam or noncondensables with alkali (usually a NaOH solution). It is a very simple and flexible method with low investment and relatively high operating expenses because of the consumption of large amounts of chemicals (Bontozoglou and Karabelas, 1993; Owen, 1984; Stephens et al., *1980).*

4.3 Steam Reboilers (A3)

This is an upstream process based on continuous condensation-reboiling of geothermal steam. The noncondensable gases are stripped together with a small quantity of uncondensed steam which acts as a carrier. The vent gases are treated in a secondary process to stabilize H_2S emissions (e.g. a liquid-redox process). There are four main seam reboiler types, such as vertical tube evaporator reboiler, horizontal tube evaporator reboiler, kettle-type and direct contact reboiler. The process can produce clean. gas-free steam hut of lower enthalpy content as compared with the raw steam. Reboilers require high total capital investment but low operating expenses (Bontozoglou and Karabelas, in press, Angulo, 1987; Awerbuch, 1985; Coury, 1985,1982; Owen. 1984; Stephens et al., 1980).

4.4 Liquid-Redox methods (B1)

This group of downstream methods is capable of absorbing H_2S from noncondensable gas streams and of producing elemental sulfur for sale or disposal. There are two subgroups of liquid-redox methods, the *vanadium-based* proccsses (e.g. Peabody Stretford, Holmes Stretford, Sulfolin, Unisulf) and the iron-bused processes (e.g. SulFerox, Hiperion, LO-CAT, Bio-SR). Liquid-Redox methods are the most widely spread processes today offering excellent H_2S removal. often reducing its level to 10 ppm or less. The most important problem they face, concern plugging (as the elemental sulfur forms particulate solids suspended in the liquid catalyst solution), and disposal of solid products especially in the case of vanadium - based processes, because of toxicity of vanadium (Dalrymple and Trofe, 1989; Dalrymple *et al.*, 1989; Satoh, 1989).

4.5 Noncondensable gas injection systems (B3)

This is a downstream method. Noncondensables are compressed, mixed wirh the brine, and reinjected into an auxiliary well. It is a relatively new technology with good prospects. *It* appears to combine some interesting advantages such as low investment. operating and maintenance costs, total removal of H_2S, high flexibility, no need for waste water treatment or combustion of exhaust gases. no sulfur precipitation or solids disposal etc. However, considerable research appears tu be necessary for investigating the consequences of reinjection into the reservoir (Hibara *et al*, 1990).

4.6 The Peabody-Xertic process (B4)

This downstream process involves the absorption of part of H_2S present in condenser off-gases by a solution containing citric acid and other citric compounds. The rest of H_2S is oxidized by air to SO_2. Then, SO_2 is introduced into the citric solution and reacting with H_2S to elemental S (Claus reaction in liquid phase). The method requires high total investment and operating cost. The citric compound solutiun is corrosive and expensive marerials of construction are needed. It is a recent abatement technique, considered effective and flexible. No toxicity problems are reported (Vancini, 1986).

6.7 Catalytic oxidation uf H_2S (B5)

This is another downstream method involving catalytic oxidation of pari of H_2S in the noncondensable guses to SO_2. Fe_2O_3 is used as catalyst. The rest of H_2S reacts with SO_2, in a gas-phase Claus reaction. H_2S is then oxidized to elemental *S*. The method was developed for desulfurization of CO_2-rich gas streams which are used for injecrion into oil reservoirs. Therefore, in its original form. it is not suitable. for geothermal applications (Madgavkar and Swift, 1983). Simplification and modification of the process could make it applicable to geothermal plans. since it appears to hold some interesting advantages.

4.8 The H_2O_2/Iron chelate process (C1)

This downstream method involves catalytic oxidation with air and H_2O_2, only of the part of H_2S which is dissolved into the condensate. to soluble sulfates or thiosulfates. Iron chelates are used as catalysts. The process has low capital requirements but rends to be abandoned because of the high consumption of chemicals. It is recommended only in cases of supplementary abatement. when the local emission regulations are very stringent (Otte. 1989).

4.9 Steam stripping (C2)

This method operates by directly contacting geothermal condensate with waste ejector steam in a counter-current stripping column. In this way, stripper operating costs are minimized. An additional abatement system is needed to remove H_2S from steam; e.g. a liquid-redox system (Domahidy and Houston, 1983).

4.10 The Burrier-Scrubber Process (D1)

This is a relatively new downstream method involving burning of H_2S in the off-gas stream to form SO_2. Scrubbing of SO_2 with condensate follows. Thus, H_2S in both the off-gas and the condensate is removed in the same process. The method requires a direct contact condenser and is suitable in cases of high NH_3 concentrations in geothermal steam. H_2S is ultimately oxidized to soluble thiosulfates. No colloidal sulfur is produced and Fouling in the cooling water circuit of the plant is not observed (Otte, 1989).

4.11 The BIOX process (D2)

In this downstream process the off-gases are compressed and mixed with condensate before entering the cooling tower. By using the reactant BIOX as catalyst, H_2S is converted to H_2SO_4. The process does not require high capital and operating expenses. No colloidal sulfur is produced and no plugging problems in the cooling water circuit are reported (Hoyer, 1991). The process is very recent and the experience gained with it seems to be limited.

5. EVALUATION OF H_2S ABATEMENT METHODS. RESULTS

By using the previously outlined methodology, a preliminary assessment of initially selected methods was carried out. This procedure led to a smaller number of qualified methods. The latter are presented below with comments concerning the criteria (a, b, c, d, e), outlined in Section 3.3, which were employed for their evaluation

A2. Scrubbing with alkali
a. Both types of condensers can be used
b. Over 90% removal of entering H_2S
c. No influence of the geothermal steam composition
d. Low capital and relatively high operating costs

A3. Steam Reboilers
a. Both types of condensers can be used
b. A removal of entering H_2S between 90% and 99%
c. No influence of the geothermal steam composition
d. High capital and low operating costs
e. A secondary process is needed to stabilize H_2S of the vent gases. For this task one of the following systems can be used.

- A Liquid Redox process (B1)
- The scrubbing with alkali process (B2)
- The noncondensable gas injection process (B3)

B1. Liquid redox processes
a. Only surface condensers can be used
b. Over 99% removal of entering H_2S
c. The NH3 concentration in geothermal fluids must be low (NH_3:H_2S<<1). For high NH_3 concentrations or when a direct contact condenser is used, treatment of condensate is necessary. For this purpose either the H_2O_2/ iron chelate process (C1) or a steam stripping process (C2) can be used.
d. The majority of liquid redox systems requires high capital expenses: therefore these methods are recommended for big units with an extended operating period
e. They are the most widely used processes today

B2. Scrubbing off-gases with alkali
a. Only surface condensers can be used
b. Over 90% removal of entering H_2S
c. As in case B1.c
d. Low capital and relatively high operating costs

B3. Noncondensable gas injection systems
a. Only surface condensers can be used
b. Almost all H_2S of the noncondensables is removed
c. As in case B1.c
d. Low capital and operating costs
e. It is a relatively new technology with good prospects. Research is necessary however, for investigating the consequences of reinjection into the reservoir

D1. The Burner-Scrubber process
a. Both types of condensers can be used but direct contact type is preferred
b. Over 98% reduction of entering H_2S
c. The process is recommended in cases of high NH_3 concentrations in geothermal steam (NH_3:H_2S>1)

Table 2. Proposed H_2S abatement methods, resulting from a preliminary procedure

Methods	Comments
A2 or B2. Scrubbing with alkali	The process is recommended for small units
A3. Steam reboilers	An additional abatement system is needed. Possible combinations: A3 → B1, A3 → B2, A3 → B3
B1. Liquid redox processes	Among the methods of this group the following are recommended: Peabody Stretford, Holmes Stretford, Biu-SR, SulFerox. One of the above methods can be adopted only under the conditions: • Use of a surface condenser in geothermal unit • Low NH_3 concentration in geothermal steam (NH_3 :H_2S << 1) Otherwise, one of the following combinations can be adopted: B1 → C1 or B1 → C2
B3. Noncondensable gas injection systems	As in case B1, process B3 can be used considering the same limitations. Otherwise, the following combinations are proposed: B3 → C1 or B3 → C2
D1. Burner-scrubber process	Process D1 is recommended in cases of high NH_3 concentration in geothermal steam (NH_3 :H_2S > 1)
D2. Biox process	The Biox process combines very interesting advantages. No limitations for using D2 are reported.

... OX process

a. Both types of condensers can be used
b. Over 95% reduction of entering H_2S
c. No influence of the geothermal steam composition
d. Relatively low capital and operating expenses
e. Recently developed process

The results are summarized in Table 2. As shown in this table, essentially six processes and seven combinations thereof *are* recommended; or nine processes and sixteen combinations, considering four options instead of one in case B1.

6. CONCLUDING REMARKS

During the last two decades many H_2S abatement processes were developed. Each one of them has some unique features as well as advantages and disadvantages. Thus, the problem of selecting an abatement system appears to be rather complicated. As geothermal fields vary and geothermal fluids are considerably different in various geographical locations, the problem becomes even more complicated. Obviously there is a great need of an assessment procedure for selecting the most appropriate abatement method for a specific application. In the present work, a preliminary assessment is made based on qualitative criteria, including condenser design, abatement system efficiency, composition of geothermal fluids, and process economics. By using the above criteria some processes *or* combination of processes are proposed. All the proposed methods are considered effective, achieving over 90% removal of H_2S entering with the geothermal fluid. The *Scrubbing with alkali* (A2), the *Steam Reboilers* (A3) and the *BIOX* (D2) processes appear to be the most flexible ones for the following reasons:

- Both types of condensers in a geothermal plant can be used
- They are not influenced by the geothermal steam composition, being capable of accommodating the changing conditions usually observed during the lifetime of a geothermal unit.

In general, the *Noncondensable Gas Injection* (B3) and the *BIOX* (D2) methods appear to have some comparative economic advantages, in that their demand for capital icvestment and operating expenses is relatively limited.

Generally, methods which demand high capital and low operating costs are more suitable for big units with an extended operating period: such methods *are* the *Steam Reboilers* (A3) and the *Liquid Redox* (B1) processes. On the contrary, methods which demand relatively low capital and high operating costs may be suitable for smaller units of relatively short lifetime. Such a method is the *Scrubbing with alkali* process (A2 or B2).

All processes of category B (downstream abatement/off-gases), e.g. B1, B2, B3, are strongly influenced by NH_3 concentration in the geothermal fluid. Adoption of a process from this group must take into consideration the following limitations:

- Use of surface condensers in the geothermal unit
- Low NH_3 concentration in geothermal steam ($NH_3:H_2S \ll 1$).

In cases of high NH_3 concentration, the *Burner-Scrubber* process is recommended.

The *Liquid Redox* methods (e.g. *Stretford, Sulfolin, Unisulf, SulFerox, Hiperion, LO-CAT, Bio-SR*) appear to be the most widely used processes today, offering excellent H_2S removal. However, their adoption may be hindered by the general limitations of methods of group B. The *BIOX* process (D2) combines very interesting advantages, with no reported limitations in its application. It must be added, however, that it is a very recent process and experience gained with it may be rather limited.

The aforementioned relatively small group of processes must be subjected to a more rigorous technical and economic assessment for final selection of the optimum process(es). Software for this task is currently under development in our Laboratory.

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