Improved recovery in H_2S–H_2O exchange process for increasing heavy water production

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GS process is the most widely used bi-thermal exchange process for production of heavy water. This paper describes how recovery of deuterium from natural water can be increased in a GS process plant, from existing limit of 19.6% to 25% by incorporating cold and hot stripper sections in the first stage exchange towers. By increasing recovery, production can be increased and operating costs reduced substantially, leading to enhanced and cheaper heavy water production from similar size plant. These concepts and novel flow sheet changes can be applied to new as well as existing plants by reassigning some of the available contacting stages to stripper sections, and still enhance production rates. They can also be applied to any other bi-thermal exchange process.

Keywords: Cold/hot strippers, deuterium, deuterium depleted water, GS process, heavy water, recovery.

NUMEROUS methods have been proposed for heavy water production of which very few showed commercial promise. The most robust and widely used process is based on chemical exchange between H_2S and H_2O operating in a pair of cold and hot towers, wherein the source of deuterium is the natural water feed. This is known as the GS process described in DuPont report DP-400 (ref. 1). This process has dominated heavy water production worldwide over decades. Recovery of deuterium, which can be stated as the fraction of *D* in natural water, and can be extracted by the process (rest goes out in the effluent stream), in a typical GS process plant remains limited to around 19.6%, due to the physical properties of fluids and energy/cost. This paper suggests improvements to GS process for enhancing recovery. A brief review of existing GS process along with introduction to theory and patented developments sets the background of this paper, and elaborates novel improvements which will increase production, reduce energy consumption per kg of D_2O produced and reduce operating costs from a similar size plant. The concepts and novel flow sheet variation are equally applicable to any bi-thermal process and could find use in other similar bi-thermal processes like H_2–H_2O exchange.

Theory of GS process and existing flow sheet arrangements

This process is based on the fact that distribution of deuterium between liquid and gas phases in H_2S–H_2O system varies with temperature. In the H_2S–H_2O system at cold conditions there is more deuterium in liquid phase as compared to hot conditions. This is a dual temperature exchange process comprising a pair of cold and hot towers in which natural water feed and H_2S gas flow countercurrent to each other. Natural water is fed to top of cold tower mass transfer section (MTS) operating at around 32°C, gas coming out of the top of cold tower is recycled to hot tower bottom where it is heated in a humidifier section, to attain hot tower temperature of 135°C. Gas coming out from the top of hot tower is fed to the bottom of cold tower where it is cooled in a dehumidifier section to attain the desired cold tower temperature. The distribution of *D* between liquid and gas has been related with an overall separation factor β. The value of β can be accurately determined for prevailing pressure and temperature conditions by knowing the equilibrium constant, solubility of H_2S in water (moles H_2S per mole liquid solution), humidity of H_2O in gas phase (moles H_2O per mole gas mixture), and relative volatilities[1,2]; thus essentially the *D* distribution between water liquid phase and gaseous H_2S phase can be related to pressure and temperature. Mathematically it can be stated that overall separation factor

$$\beta = X(1 - Y)/Y(1 - X)$$
$$= X/Y, \text{ at low concentrations like those prevailing in first stage since } (1 - X) \text{ and } (1 - Y) \text{ are very nearly equal to one,}$$

where *X* is mol fraction of *D* in liquid phase and *Y* is mol fraction of *D* in gas phase. Hence, $Y = X/\beta$. This gives the equilibrium line at low concentrations. Typical values of β at cold and hot tower conditions are around 2.267 and 1.595 at 21 bar pressure.

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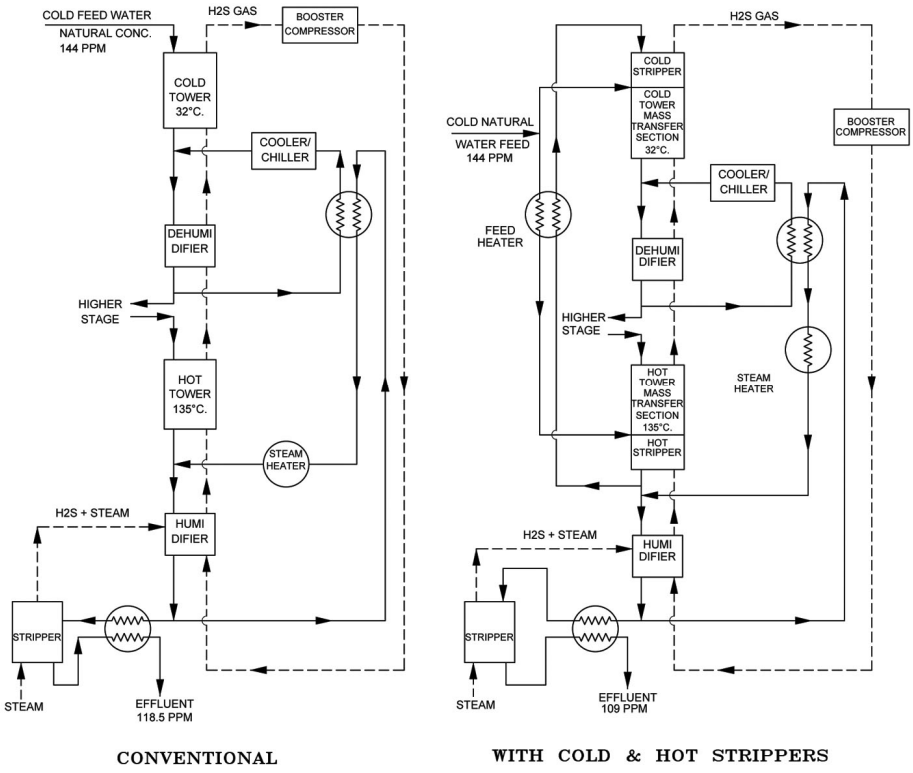

Figure 1. GS process plant flow arrangements.

This leads to the fact that if a stream of water is flowing first down a cold tower counter-current to H_2S gas, and then down a hot tower with the gas in closed loop recirculation, then D gets absorbed from gas in the cold tower and gets stripped from liquid in the hot tower. Thus D gets concentrated at the bottom of cold tower and top of hot tower. Portion of cold tower bottom liquid is then withdrawn as product for further enrichment in subsequent stages and returned here at a lower D concentration.

Dual temperature GS process operates at 20 bar gauge pressure at a cold tower temperature of 30–32°C and at a hot tower temperature of up to 135°C. The spread of temperature sets the limit on recovery. The higher the temperature difference between cold and hot towers along with operating pressure, greater is the recovery. Temperature limits are fixed by practical considerations. While lower cold tower temperature is limited by formation of a solid hydrate which chokes the lines, heat exchangers and trays, limitation on higher hot tower temperature arises from increasing thermal energy needs, without a corresponding gain in production, as well as need for larger equipment. The equilibrium lines of cold tower and hot tower are so close to each other that even with the approach to equilibrium being greater than 98%, theoretical maximum recovery is limited to around 19.6%. Thus if there were 100 atoms of deuterium in feed water, then only 19.6 atoms can be extracted and taken further for enrichment; balance 80.4 atoms will go out along with the effluent stream.

Well managed heavy water plants operate with specific energy of 28–30 GJ/kg of D_2O as heat and with average recovery of 18–19% over the entire year of operation. The energy used as electricity accounts for nearly 8.5 GJ/kg and thermal energy supplied as steam contributes 20.5 GJ/kg. Due to high energy requirement in GS process, operating costs are practically the energy costs.

A schematic of the first stage of a ‘conventional GS process’, is shown here along with the arrangement of flows in Figure 1.

The major energy consumption in GS process is due to heating of gas in hot tower. Though heat is partially recovered between recirculating streams of direct contact heat transfer sections, energy requirements still remain high. While temperatures vary in heat transfer sections, there is no substantial variation in mass transfer sections.

Recovery of deuterium from natural water feed can be given as

$$\text{Recovery} = (X_F - X_W)/X_F$$
$$= D \text{ content of (feed – waste) streams/}$$
$$D \text{ content of feed stream,}$$

subscripts F and W denote feed and waste streams. This value at selected operating conditions of 21 bar, and 32/135°C temperature remains limited to around 19.6%.

In a conventional plant without cold and hot strippers, natural water feed is taken to the top of cold towers. Deuterium content of this water is lower than natural water due to dissolved H_2S. The H_2S gas leaving top of cold tower will be in close equilibrium with this feed water, with certain approach to equilibrium (which is nearly 0.99). Now this gas is pumped to bottom of hot tower and heated to acquire hot tower temperature conditions and gets saturated with hot effluent water. As temperature increases, humidity increases, and solubility decreases. Increase of humidity causes rise in *D* concentration of H_2S gas mixture. The effluent water leaving hot tower bottom is in certain equilibrium with the hot gas (approach to equilibrium being close to 1). Hence concentration of deuterium in effluent water can be worked out. Difference between deuterium content of feed and effluent corresponds to recovery. Depending upon the requirement of building up concentration of deuterium at bottom of cold tower, the required number of contacting stages is to be provided in cold tower mass transfer section. From cold tower bottom, a product liquid stream is taken to a higher stage and depleted stream is returned to the top of hot tower. Depending upon the concentration prevailing here, the required number of contacting stages is provided in hot tower mass transfer section. Normally the first stage is designed for building up the deuterium concentration four fold.

Equilibrium relationship data are available as a function of pressure and temperature. They correlate to provide distribution of deuterium between gas and liquid phases. The distribution coefficient can be taken nearly constant in each section since variation of pressure and temperature in each mass transfer section is rather insignificant and the variations also can be easily accounted in modern day calculations. There is substantial variation in temperature in heat transfer sections (humidifier and dehumidifier sections); however these are for heating and cooling of gas and there are no large mass transfer effects in these sections, in fact in these sections liquid gets mixed due to recirculation from bottom to top.

Many attempts have been made to increase recovery and production as described below.

Improvements in GS process proposed so far

AEC Research and Development Report, by Burgess[3], predicts 10% increase in production if extra feed is given to hot tower at an appropriate tray, in addition to normal feed input to cold tower in the first stage, when supplementary feed is about one third of the normal feed to cold tower. This would result in an increase in effluent concentration; however, increase in production due to extra feed overrides the decrease in recovery. For a production gain of 10%, recovery decreases from 18.23% to 14.24%. It has been reported that higher production gains beyond 11% are possible with large increase in total water processed, but are not considered economical. It is inevitable that overall thermal energy needs will also increase, as more heat would be lost with increased quantity of effluent.

The US patent by Babcock[4] claims a potential for 11.2% increase in production by withdrawing and introducing 50% of the feed from upper portion of CT into lower portion of HT towards bottom. Total water feed is increased by 50%, and recovery decreases, though an overall production gain of 11.2% is claimed. Another US patent by Pauluis[5] describes an invention where the entire fresh feed is taken to hot tower. This has an added advantage that cold natural feed is used to recover heat from cold tower recirculation stream; this heat is returned to the process. The invention claims a production gain of 5.7–6.5%, with steam savings.

Initial plants on this process were setup by US and Canada. India, Romania, Pakistan, Iran, Russia and possibly China have also setup plants based on this process. However, no heavy water plants with these changes incorporated are known to have been built in US, Canada or India (information is not available from other countries). While the theory along with suggested improvements has created interest, and analysed in detail worldwide (results of detailed simulations have been reported)[6], no operating data on enhanced recovery or enhanced production are available.

Concept of cold/hot strippers for increasing recovery

All improvements in GS process, proposed so far, show increase in production rates with loss of recovery. In an attempt to achieve highest possible recovery, concept of incorporation of cold/hot strippers into the traditional GS process was applied, analysed and presented here. The improvements suggested here enhance recovery to 25% and result in production gain of around 28%.

Heavy water plants operating on GS process have approach at the cold tower top and hot tower bottom very close to 0.99. This approach decides the requirement of ideal stages. As the usual design approach is close to 0.99, recovery cannot be increased further in a traditional GS process, for a given temperature difference between cold and hot towers. Improvements suggested here lead to process intensification by manipulation of recirculation of lower concentration liquid streams and by enhancing gain per tray at effluent end.

For optimum placement of operating lines, the ratio of slopes of equilibrium line to operating line is kept equal in cold and hot tower mass transfer sections (slope of the operating line is equal to L/G – ratio of liquid to gas flow rates). It also leads to nearly equal number of ideal stages in both cold and hot tower mass transfer sections, and

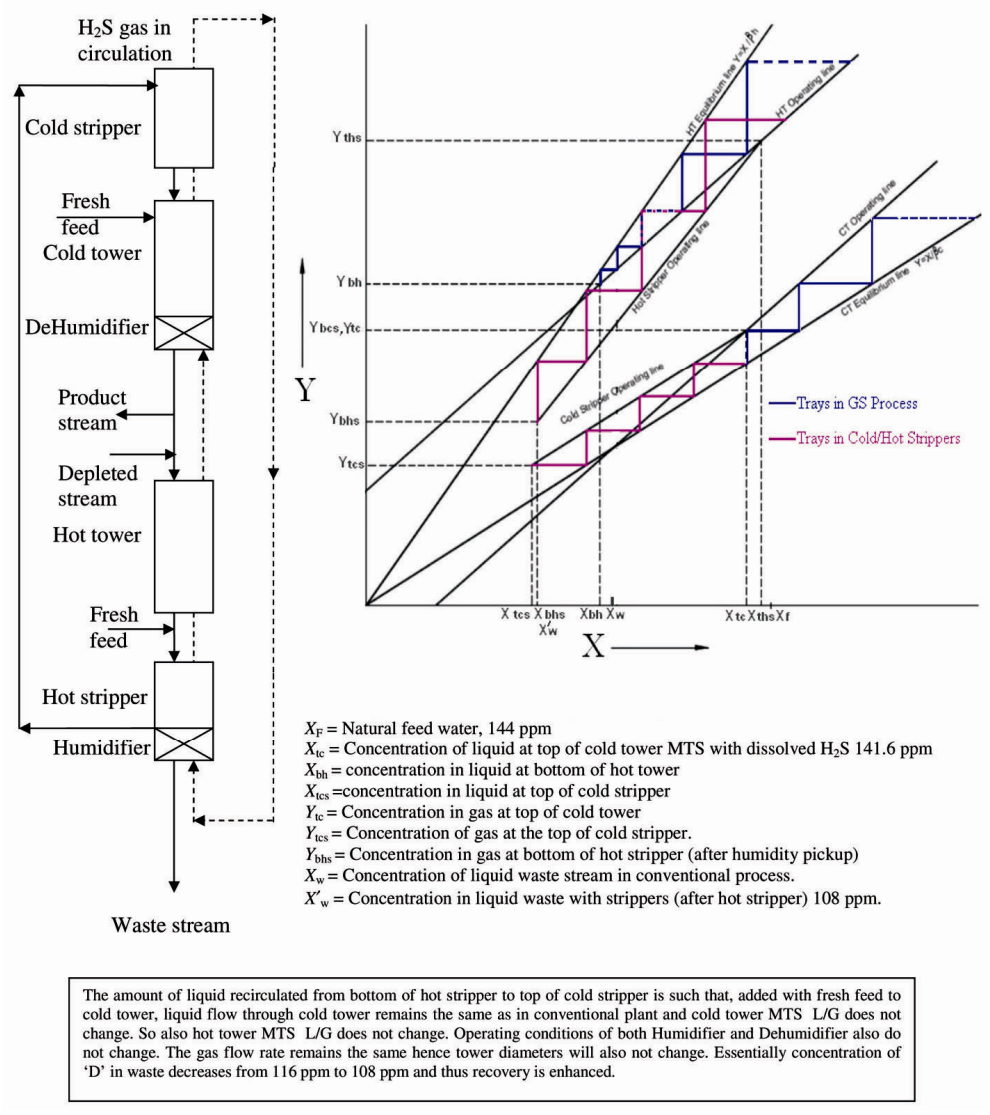

Figure 2. Reduced waste concentration with cold and hot strippers in GS process.

also maximum recovery (called optimum L/G). After fixing the gas flow rate, corresponding to maximum tower capacity, liquid flow to cold tower mass transfer section can be varied independently, to set the ratio of liquid to gas flows (popularly called L/G) in cold tower. Then L/G of hot tower gets fixed based on prevailing humidity and solubility.

Concentration gain per tray at cold tower top and hot tower bottom is low. If operating lines at these low concentrations are driven away from the equilibrium lines by changing their slope (by changing the liquid flow rate as full gas flows anyway for maximizing the feed processing), the driving force for deuterium transfer between the gas and liquid increases and results in a lower concentration of deuterium in effluent water. This concept has been incorporated into the GS process flow sheet to arrive at the cold and hot strippers.

A novel flow sheet arrangement has been worked out, in which fresh feed is sent partly to cold tower mass transfer section and partly to hot stripper. From bottom of hot stripper the liquid is recirculated to top of cold stripper after temperature adjustment, in such a manner that total liquid loading in mass transfer section of cold tower corresponds to optimum L/G, as in the conventional GS process.

Entire gas from the top of cold tower mass transfer section enters cold stripper. At top of cold stripper gas comes into contact with depleted *D* liquid recycled from hot stripper bottom; hence concentration of deuterium in leaving H_2S gas is lowered. Lower L/G is maintained in cold stripper to take its operating line away from equilibrium line. The gas flowing through cold stripper gets further depleted in deuterium while liquid gets enriched. As feed concentration is reached, fresh feed is taken in.

Table 1. Summary of results with 144 ppm of $D/(D + H)$ in feed water

	Recovery from natural water (%)	Ideal stages assigned	Expected specific energy consumption, GJ/kg of D_2O produced	Concentration $D/D + H$ at hot tower bottom, ppm by mol
Traditional GS process	19.6	Cold tower – 35 Hot tower – 37	29.8 GJ/kg	116
GS process with cold/hot strippers, suggested design of a new plant; by adding 5 ideal stages in cold and hot towers each to create the stripper sections	25	Cold stripper – 5 Cold tower – 35 Hot tower – 32 Hot stripper – 10	<18 GJ/kg*	108
Existing GS process plants incorporating cold/hot strippers by sacrificing part of mass transfer section trays	24	Cold stripper – 5 Cold tower – 30 Hot tower – 26 Hot stripper – 9	24**	109.4

*Coupled with certain other engineering changes, otherwise 23.4 GJ/kg. **In the existing plants adopted to create cold and hot strippers.

Along with some fresh feed the liquid from cold stripper joins and flows to the cold tower mass transfer section to maintain optimum L/G in the cold tower mass transfer section as in the conventional plant.

The corresponding liquid and gas flow rates continue into hot tower mass transfer section. Here again optimum L/G is maintained, as in the conventional GS process. At the bottom of hot tower L/G is increased by adding fresh feed into the column at matching concentration, which takes operating line of hot stripper away from equilibrium line (Figures 1 and 2). This results in reduction of deuterium concentration in the liquid to a lower value as it travels down the hot stripper. A part of this liquid is recycled to cold stripper completing the cycle. The amount of liquid recirculated from the bottom of hot stripper to top of cold stripper is such that, added with fresh feed to cold tower, liquid flow through cold tower mass transfer section remains the same as in conventional plant and the L/G of cold tower mass transfer section does not change. Again L/G of hot tower mass transfer section remains the same as in conventional flow sheet. Operating conditions of both humidifier and dehumidifier also do not change from conventional flow sheet.

The fresh feed is distributed between cold tower and hot stripper. The fresh feed to hot stripper is preheated with recycled liquid being fed to cold stripper. The recycled liquid from hot stripper is drawn before humidifier. This keeps the same liquid loading in humidifier as in conventional process.

Compared to a conventional plant the design of both mass transfer and heat transfer sections of cold and hot towers does not change at all. One additional pumpset has to be added for recirculating the hot stripper bottom liquid. Five additional ideal stages each are to be provided each in both cold and hot towers to incorporate the strippers. Total feed water remains the same, steam consumption does not change, and electricity consumption increases insignificantly corresponding to one pump set.

A schematic along with operating lines is depicted in Figure 2 (pumps and gas boosters are not shown).

All arguments here have been stated for feed/waste end in first stage where deuterium concentrations are very low (110–150 ppm). Hence both operating and equilibrium lines can be taken as straight lines. For higher stages equilibrium line gets curved; details of which are available in ref. 1.

Calculations show that in a conventional plant without stripper sections, approach to equilibrium at top of CT MTS with typical 35 ideal stages is 0.990744, which decreases to 0.9839 if number of ideal stages is reduced to 30. This has an effect of increasing concentration of deuterium in HT MTS outgoing liquid, by 1.45 ppm by mole, thus causing a loss of 1% in recovery. Desired concentration build-up can be achieved at bottom of CT (594 ppm taken in these calculations) in both cases. Thus existing plants can be upgraded by converting part of MTS to stripper sections and realize production gains. Results have been summarized for all three cases.

Distribution of total fresh feed between cold tower and hot stripper is approximately 42% and 58%. With 144 ppm D content of fresh feed water, waste concentration at hot stripper bottom shall be 108 ppm. Calculations using our property data-base have shown that by the above arrangement, recovery from natural water increases to 25% (Table 1), thus there is a production gain of 28%. This improvement coupled with various other improvements can give a plant design which can produce heavy water with only 18 GJ/kg energy consumption. The suggested changes can also be incorporated in existing plants by sacrificing few trays of cold and hot towers for creating the stripper sections, and realize recovery gains.

Production of deuterium depleted water

There is another interesting option. This cascade with cold and hot strippers can be operated with another set of

flow rates to achieve 95 ppm *D* content of waste stream. There are reports that deuterium depleted water (DDW) is useful for treatment of cancers and type-II diabetes mellitus[7,8]. Such a cascade can be further engineered to produce DDW of 90 ppm or even lower and can make abundant quantities of DDW available cheap for huge societal benefits.

Conclusions

Increase of recovery to 25% of feed stream in the GS process is a significant development which makes it possible to produce heavy water cheaper. Incorporation of cold and hot stripper does not increase energy consumption as gas flow rate does not change, and utilities required for circulation, heating and cooling the gas remain the same.

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