

## HOT GAS STRIPPING OF SIMULATED IN SITU OIL SHALE RETORT WATER

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### Introduction

The large quantity of water produced by in situ oil shale retorting processes poses a potential pollution problem of significant magnitude. Waters collected from experiments conducted in the Laramie NTU type simulated in situ retorts have been examined (1) and have been shown to contain large concentrations of organic and inorganic species that could pollute the environment if not removed prior to disposal of the water. A study by Cook (2) of water produced from the Tosco II process revealed the presence of a variety of organic materials that could also harm the environment. Further, Hubbard (3) studied the process water produced by the Bureau of Mines gas combustion retort operated at Rifle, Colorado, and the water produced from the in situ retorting process near Rock Springs, Wyoming. He found that the waste water produced by both processes contained essentially the same components although in different quantities. Hubbard suggested two slightly different schemes to treat the waste water. One was to first contact the water with lime followed by activated carbon, a cation exchange resin, and finally an ion exchange resin. In his second scheme he suggested that the waste water should first be contacted with activated carbon and then with lime and the ion exchange resins. He concluded that it may be possible to recover ammonia and ammonia salts in addition to purifying the water.

A number of other investigators have also studied various retort waters and have found essentially all the species identified in the work of Jackson et al. (1). Using the assumption of Harak, Long, and Carpenter (4), that one barrel of water is produced with each barrel of oil, a 50,000 barrel per day in situ process would produce 2352 acre feet of water annually. Consequently, the study of methods to treat retort water is very important to the development of a viable shale oil industry.

The most prevalent species found in the retort water are the ammonium ions and the carbonates. Because they are present in large quantities, 13,000 ppm ammonia and 45,000 ppm carbonates, they must be dealt with prior to the treatment of retort water by either adsorptive or ion exchange techniques. A search of the literature (5-19) revealed that the petroleum industry routinely uses hot gases, particularly steam and flue gases, to strip sour water containing  $H_2S$  and  $NH_3$ . Because of the success of the petroleum industry in removing  $H_2S$  and  $NH_3$ , the removal of ammonium ions and carbonates from retort water appears feasible and will be addressed in this study.

### Experimental

The equipment used in carrying out the experimental study consists of a stripping column equipped with fluid handling devices, heat transfer equipment, and temperature and pressure monitoring sensors; a schematic of the apparatus is shown in Figure 1. The liquid feed is introduced into the column with a variable speed diaphragm type metering pump and the flow rate is measured with a rotameter. Prior to entering the column, the feed water flows through a three zone electrical resistance furnace where it is heated to the desired temperature.

The gas system is presently set up for two types of gases; one is steam supplied by a miniature steam generator, the second is a bottled gas, such as compressed nitrogen or air. The gas also flows through an electrical resistance furnace where

heat is transferred into a twenty foot long section of tightly coiled stainless steel tubing. From the furnace, the stripping gas passes through a rotameter and is injected into the bottom of the column where it flows upward, countercurrent to the downward flowing liquid feed. The gas exits from the top of the tower and passes through a small water cooled heat exchanger, then through two water traps and finally is vented to the atmosphere. The stripped water flows from the bottom of the column, through another small heat exchanger and is collected for subsequent analysis.

Temperature measurements are made by inline thermocouple connections at all inlet and outlet ports on the column as well as on the heat exchangers. Control of the inlet temperatures of the gas and liquid streams is made by two separate temperature controllers. The temperatures are read to  $\pm 2$  degrees Fahrenheit from a digital readout device connected in parallel to a millivolt recorder. The absolute pressure is monitored with a pressure transducer connected to a digital millivolt output device.

The column itself is constructed of heavy wall, two inch NPS glass pipe made up in six sections of varying lengths for a total height of nine and one half feet; the sections are flanged together using a Teflon type gasket material. The packing height can be varied by using one of four different liquid injection ports along the column. The gas enters the bottom of the column just above the point at which the liquid exits. The gas passes upward through the irrigated packing and is removed from the top of the column. Connections from the 1/4 inch stainless steel tubing and the 3/8 inch glass column ports are made by a combination of flexible stainless steel hose and a special Teflon reducing union. In order to obtain representative data, it has been suggested that the column diameter be approximately eight times greater than the packing size. Consequently, the two inch column used in this study is packed with 1/4 inch Intalox saddles. To decrease water entrainment, four inches of Pyrex glass wool is packed into the top of the column. Because of the ineffectiveness of dry packing in distributing the liquid feed across the column, a flow distributor has been installed in all liquid inlets.

The effects of several key variables on the desorption rates of ammonia and carbon dioxide from a simulated retort water have been measured using the bench scale stripper column. In this study a number of parameters are evaluated: the effects of liquid and gas flow rates, the temperature of the stripping gas and retort water, and the packing height. The effects of pH, lime addition, and comparisons between actual and simulated retort water are presently underway, but as yet have not been completed.

Water flow rates varied over the range of 430 - 1,300 lb/hr ft<sup>2</sup> while gas rates were varied from 60 - 150 lb/hr ft<sup>2</sup>. The liquid to gas ratios varied from 6 - 35 SCF/gal of feed, and are within the range used to strip comparable quantities of H<sub>2</sub>S and NH<sub>3</sub> from sour water refinery streams. The column was maintained at a constant temperature for each run; the stripping temperatures were varied from 160 - 200 °F. The packed height available for stripping can be set at: 0.98, 2.79, 4.35, or 7.21 feet by changing the position of the water feed. Flooding characteristics of the two inch column were such that the approach to flooding varied from 12 to 20 percent. These values were maintained to keep entrainment of retort water in the gas to a minimum.

The water used to date has been a simulated retort water containing only ammonium bicarbonate. The pH of this water was that of the natural pH of the solution, 7.8 - 8.0 and the average concentrations of NH<sub>3</sub> and HCO<sub>3</sub><sup>-</sup> were 11,000 ppm and 43,000 ppm respectively.

## Results

Several operating parameters such as: temperature, liquid and gas flow rates,

and column height, were evaluated to determine their effect on the stripping of a simulated retort water. Equilibrium data for the ternary system  $\text{NH}_3$ ,  $\text{CO}_2$ , and  $\text{H}_2\text{O}$  presented by Van Krevelin, et al., (20) and Badger and Pexton (21), show that  $\text{CO}_2$  has a partial pressure higher than  $\text{NH}_3$  in the vapor phase above the aqueous solution containing these compounds. The conclusion that may be drawn by examining this equilibrium data is that it is much more difficult to strip  $\text{NH}_3$  from solution than  $\text{CO}_2$ . When compared to  $\text{CO}_2$ , the removal of  $\text{NH}_3$  requires: higher temperatures, larger gas to liquid flow rates, and/or taller columns.

The relative effects of the liquid flow rate on the removal of bicarbonate ions,  $\text{HCO}_3^-$ , are shown in Figure 2 and the corresponding graph for the removal of  $\text{NH}_3$  is given in Figure 3. For this set of runs, the temperature was held constant at  $200^\circ\text{F}$  and the average gas flow was  $165 \text{ lb/hr ft}^2$ . This gas rate corresponded to about 11, 20, and 40 SCF/gal of solution feed. As can be seen, the smallest liquid flow of  $431 \text{ lb/hr ft}^2$  corresponded to the lowest solution concentration. The gas to liquid ratio of 40 SCF/gal corresponds to the maximum gas flow used by the petroleum industry to strip  $\text{H}_2\text{S}$  and  $\text{NH}_3$  from sour water. For a flow rate of 20 SCF/gal, the concentrations of both  $\text{NH}_3$  and  $\text{HCO}_3^-$  are higher than at the highest flow ratios. From the figure, it is seen that the  $\text{HCO}_3^-$  concentration initially ranges from 35,000 to 47,000 ppm by weight and rapidly decreases to 250 - 1,300 ppm. The  $\text{NH}_3$  has an initial concentration of 15,000 ppm and drops to 3.7 ppm for the lowest liquid flow rate after passing through 7.2 feet of packing.

A situation similar to the one above can be seen in Figures 3 and 4. In these graphs the effects of a 40 percent gas rate increase at the constant liquid flow rate of  $431 \text{ lb/hr ft}^2$  are illustrated; the gas to liquid ratios are 29 and 41 SCF/gal. Note that a 40 percent gas rate increase does not affect the concentrations as much as a change in the column height. At a packed height of only 0.98 feet, the  $\text{HCO}_3^-$  concentration is reduced from 45,000 ppm to approximately 21,500 ppm. The  $\text{HCO}_3^-$  concentration is further reduced to about 9,000 ppm after 2.69 feet of packing and to about 4,000 ppm after 4.35 feet of packing. The final bicarbonate concentration leaving the bottom of the column is about 1,000 - 2,000 ppm. These data indicate bicarbonate removal in the range of 98 percent at only  $180^\circ\text{F}$  with a corresponding ammonia removal of 97 percent. At the same gas to liquid ratio of about 40 SCF/gal, an increase in the temperature to  $200^\circ\text{F}$  permits removal of greater than 99.5 percent  $\text{HCO}_3^-$  and 99.9 percent  $\text{NH}_3$ . Figure 6 illustrates the effects of temperature on the quantity of  $\text{HCO}_3^-$  that remains in solution at a fixed gas to liquid rate of 11 SCF/gal. At this gas to liquid ratio the chemical equilibrium shifts with the increase in temperature from  $180^\circ$  to  $200^\circ\text{F}$  to provide a larger driving force for mass transfer. The equilibrium change with increasing temperature results in higher gas partial pressures of  $\text{NH}_3$  and  $\text{CO}_2$  for a given liquid composition. At the higher temperature, a shorter column could be used to produce a given effluent composition.

### Conclusions

This study demonstrates that  $\text{NH}_3$  and  $\text{CO}_2$  can be effectively removed from water by hot gas stripping. At a stripping temperature of  $200^\circ\text{F}$  and a stripping ratio of 40 SCF/gal, the ammonia concentration was reduced from 11,000 ppm to 3.7 ppm and the bicarbonate concentration was reduced from 47,000 ppm to 220 ppm. These values reflect a removal of about 99.5%.

The components introduced into the stripping gas could be removed by a number of methods including incineration and adsorption. Assuming an  $\text{NH}_3$  concentration of 13,000 ppm in a process that produces 50,000 barrels of water per day, the potential ammonia recovery would be about 41,600 tons per year. Because of the value of ammonia to the fertilizer industry, its recovery should be economically feasible.

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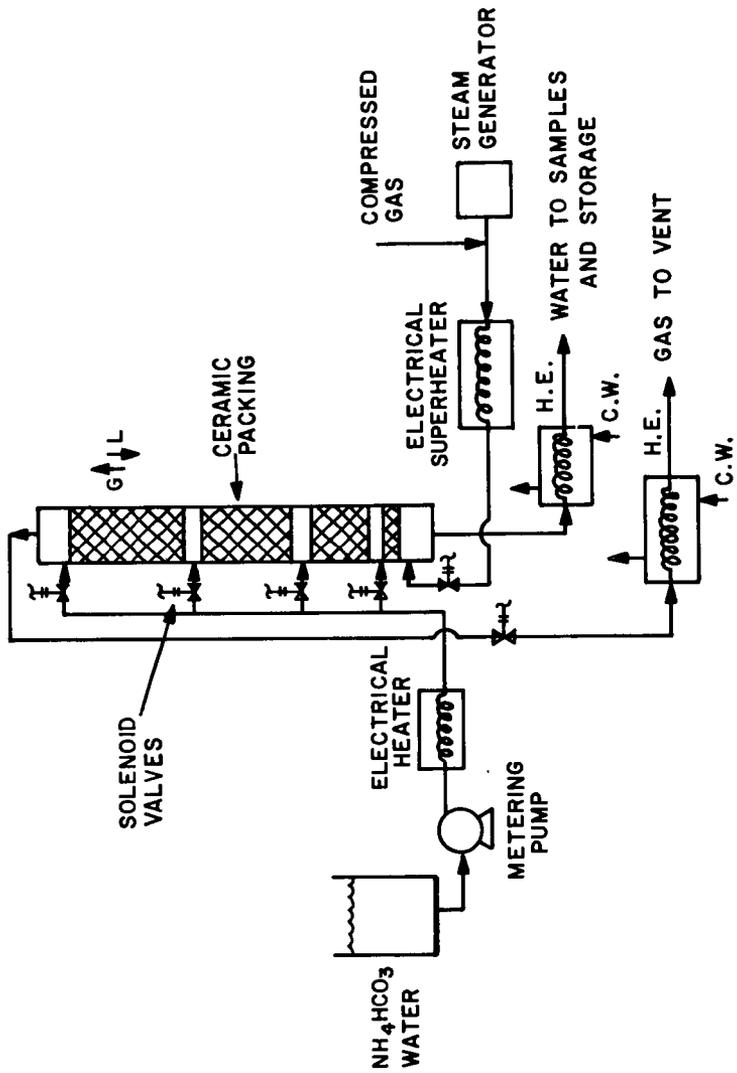


FIGURE I. EXPERIMENTAL EQUIPMENT

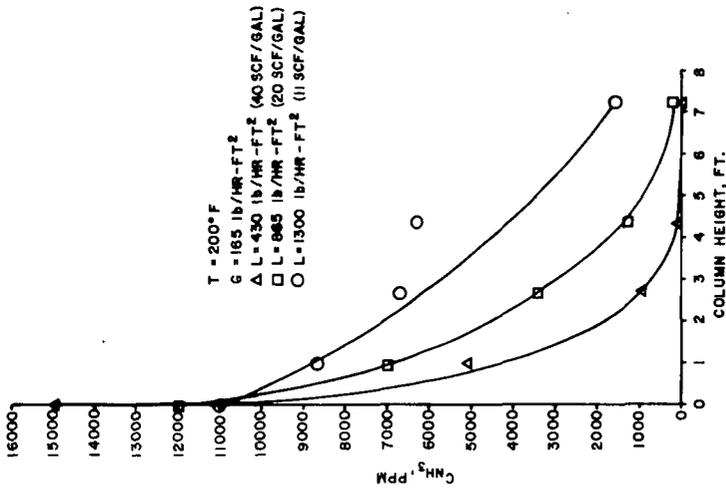


FIGURE 3. EFFECT OF WATER FLOW RATE ON AMMONIA EFFLUENT CONCENTRATION AS A FUNCTION OF COLUMN HEIGHT.

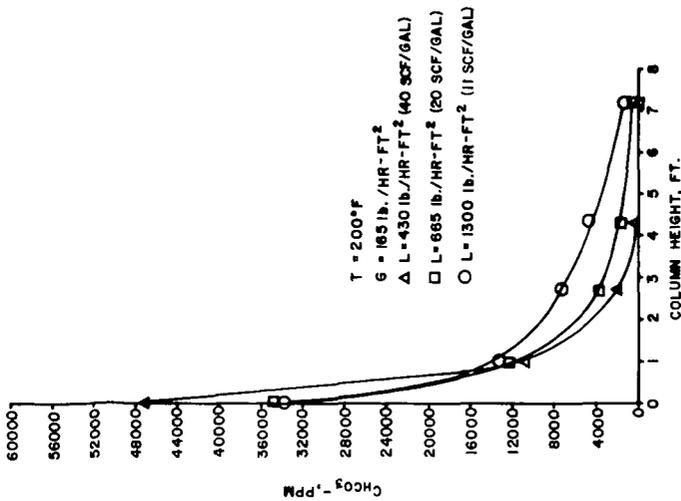


FIGURE 2. EFFECT OF WATER FLOW RATE ON BICARBONATE EFFLUENT CONCENTRATION AS A FUNCTION OF COLUMN HEIGHT.

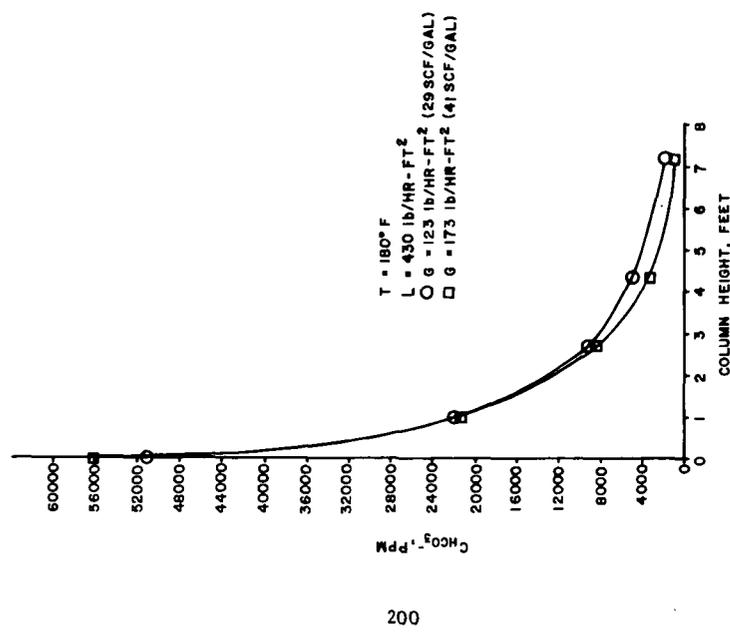


FIGURE 4. EFFECT OF GAS FLOW RATE ON BICARBONATE EFFLUENT CONCENTRATION AS A FUNCTION OF COLUMN HEIGHT.

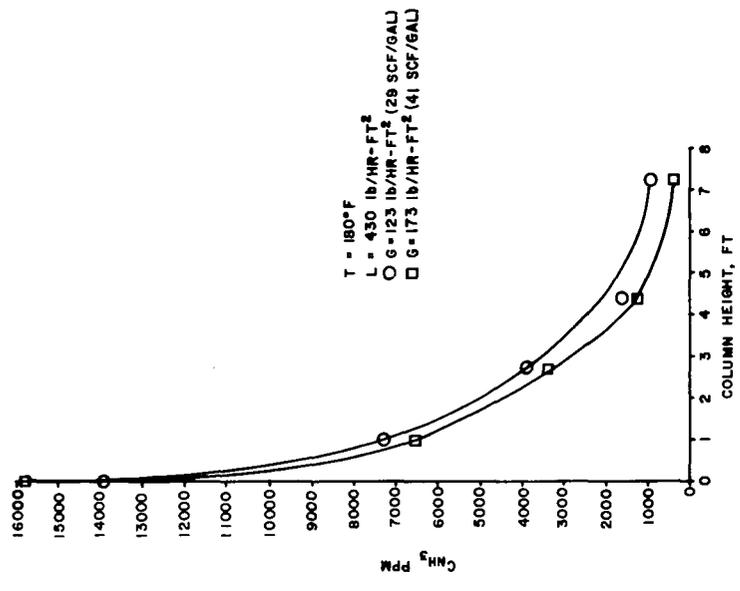


FIGURE 5. EFFECT OF GAS FLOW RATE ON AMMONIA EFFLUENT CONCENTRATION AS A FUNCTION OF COLUMN HEIGHT.

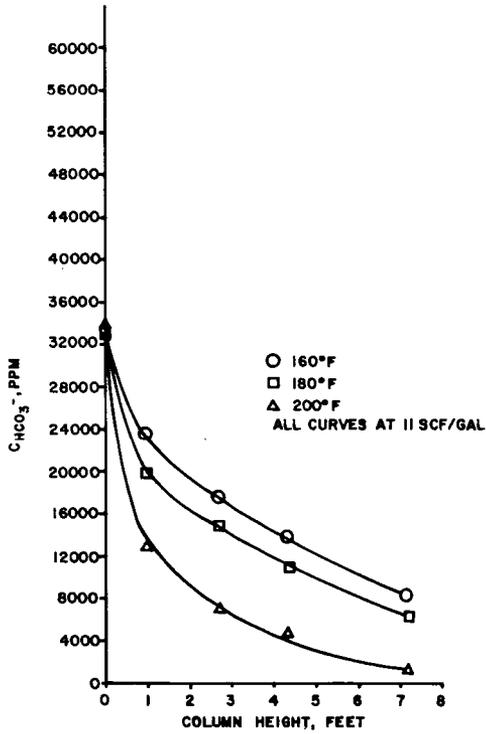


FIGURE 6. EFFECT OF TEMPERATURE  
 ON BICARBONATE EFFLUENT  
 CONCENTRATION AS A  
 FUNCTION OF COLUMN  
 HEIGHT.