HOT GAS STRIPPING OF OIL SHALE RETORT WATERS

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ABSTRACT

Hot gas stripping of ammonia and carbon dioxide from three different types of oil shale retort waters was investigated in a packed column. The stripping operation was carried out by countercurrent liquid-gas contact over a temperature range of 82.2 to 104.4°C (180 to 220°F) in a glass column packed with Intalox Saddles. The stripping rates were determined by measuring the liquid concentration of ammonia and carbon dioxide at three different column heights and three different stripping temperatures for three inlet gas flow rates (flooding velocities).

Both ammonia and carbon dioxide could be effectively removed from solution at 82.2, 93.3, and 104.4°C (180, 200, and 220°F) at a variety of flow conditions for Omega-9 and OXY-6 retort waters. Although hot gas stripping significantly reduced the ammonia and carbon dioxide in Run-17 retort water, the stripping process is less effective for this type water than for the other two studied in this work at comparable stripping conditions.

INTRODUCTION

An in-situ oil shale development program requires consideration of the water produced with the oil during retorting. Studies conducted at the Laramie Energy Technology Center (LETC) for Colorado and Utah shale, showed that approximately one barrel of water is produced for every barrel of oil (Jackson et al. 1975, Harak et al. 1970). Consequently, the development of methods to utilize oil shale retort waters is an important aspect of the development of a shale oil industry. Retort waters contain large quantities of inorganic and organic compounds including significant amounts of carbonates and ammonia. These high solute levels allow few options for direct utilization of retort waters. However, their presence represents a potential source of commercially valuable by-products that can be recovered during the water treating process.

Because of the success of the petroleum industry in using hot gases to strip hydrogen sulfide and ammonia from refinery waste waters, (Peoples et al. 1972, Annessen et al. 1971, Klett 1972, Elkin et al. 1951, Hull 1958, Brunet et al. 1972, Rodrigues 1974, and Beychok 1968), hot gas stripping appears to be a feasible method for treating retort waters. In this study the hot gas stripping of ammonia and carbon dioxide from three different oil shale retort waters was investigated in a packed column. Stuber et al. (1978) noted that sulfide was not detected in the retort waters in which they studied. Thus sulfide stripping was not addressed in this work. The stripping characteristics were determined as a function column height, stripping temperature, and gas and liquid flow rates. Concentrations of ammonia, carbon dioxide, and total organic carbon (TOC) were measured before and after stripping.

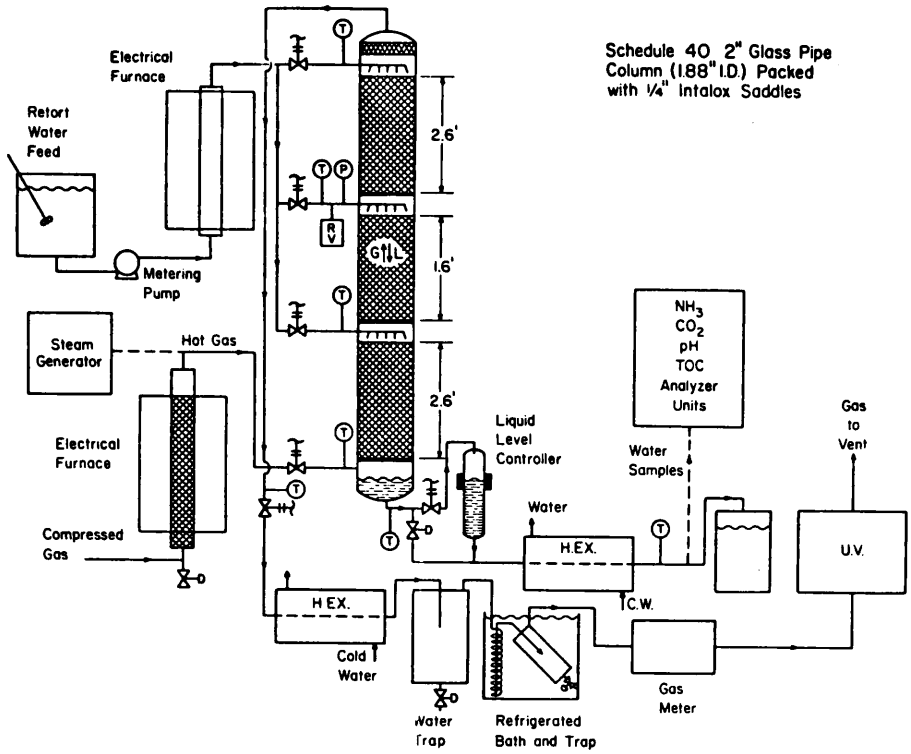

FIGURE 1. Experimental Equipment Flow Diagram

EXPERIMENTAL

Three types of retort water were used in this work. One was obtained from the true in-situ oil shale combustion experiment conducted by the Laramie Energy Technology Center at Rock Springs, Wyoming and is denoted as Omega-9. This water has been characterized by Fox et al. (1978) and was found to be relatively low in organic carbon because of ground water incursion. The second type of retort water was obtained from the 150 ton oil shale retort located in Laramie, Wyoming from retorting a Colorado shale and is denoted as Run-17. The third type of water was obtained from the Occidental Oil Shale Corporation's Retort 6 at Logan Wash near DeBeque, Colorado. The latter two waters were characterized by Ahern (1982).

Apparatus

A packed stripping tower was the principal piece of equipment in this study. It was designed to operate over a temperature range of 23.9 to 121.1°C (75 to 250°F) with liquid flow rates variable from 488.2-7323.6 kg/h-m^2 (100-1500 lb/h-ft^2) and with gas flow rates ranging from 0-1.12 SCM/L (0-150 SCF/gal) of liquid feed. The column, which was 2.9 m (9.5 feet) in length, was constructed from a 5.08 cm (2.0 inch) diameter, schedule 40 glass pipe. It was randomly packed with 0.635 cm (¼ inch) Intalox saddles to provide liquid distribution and gas-liquid contact inside the tower. The stripping height could be set at 79.2, 128.0, or 207.3 cm (2.6, 4.2, or 6.8 feet) by changing the position of the water feed. Two electrical furnaces were used, one for heating the inlet gas stream and the other for heating the inlet liquid stream to the column. Two heat exchangers were used to cool the hot liquid and gas streams leaving the column to room temperature. A silicone coated electrical heating tape was wrapped around the column to maintain isothermal stripping conditions. A calibrated pressure transducer located midway in the column was used to monitor the column pressure; the pressure of the hot gas entering the column was also measured. Steady state operating conditions were determined by using an ultraviolet spectrophotometer to monitor the concentration of the gas leaving the column. A flow diagram of the experimental apparatus is shown in Figure 1. Entrainment of liquid droplets in the exiting gas phase was eliminated by placing four inches of pyrex glass wool in the top of the column. The glass wool, which was chemically inert, provided a substantial surface area for removing water droplets from the gas phase.

Procedure

The stripping operation was carried out by countercurrent gas-liquid contact. The liquid stream was first preheated to the desired temperature and then pumped to the top of the column at a specified flow rate. The gas stream was heated to the desired operating temperature and presaturated with water before it entered the bottom of the column. When steady state operating conditions were attained, effluent liquid samples were taken for each stripping height. The pH and the concentrations of the three major species ammonia, carbon dioxide, and total organic carbon (TOC) were measured for each sample. The concentration of ammonia was determined by using the distillation-acidimetric method ASTM D1426A. Total CO_2 was determined titrimetrically (ASTM D513), and TOC was measured with an Oceanography International total carbon infrared analyzer by using the ampule technique.

RESULTS AND DISCUSSION

Because of the differences in amounts of ammonia, carbon dioxide, and TOC found in the various retort waters, three different types of water were selected for study in this project. Stripping experiments were performed at 82.2, 93.3, and 104.4°C (180, 200, and 220°F) under isothermal conditions using inlet liquid flow rates that ranged from 1801.6 to 3827.8 kg/h-m^2 (369 to 784 lb/h-ft^2) and gas rates that ranged from 1269.4 to 3583.7 kg/h-m^2 (260 to 734 lb/h-ft^2) of column cross section. Column flooding velocities ranged from 46 to 88%. Concentrations of the three species: TOC, ammonia, and carbon dioxide were measured before and after stripping, and were plotted as a function of column height, temperature and flow rate. In order to determine the effects of process conditions on the stripping rate, 27 runs were made for each retort water.

The first part of this study was carried out using the Omega-9 retort water which had initial concentrations of 3983 mg/L ammonia, 8006 mg/L carbon dioxide, and 840 mg/L TOC. The effluent concentrations for the three species are presented in Table 1 as a function of flooding velocity. For the 104.4°C (220°F) stripping temperature, and the 2.07 m (6.8 ft) column height, essentially all of the ammonia was removed from the retort water at all three flooding velocities. At this same temperature the amount of carbon dioxide was reduced from 8006 mg/L to about 1700 mg/L for each flooding velocity and the TOC concentration was reduced from 840 mg/L to 430 mg/L.

The effluent concentrations are shown as a function of column height in Figures 2, 3, and 4 for the three stripping temperatures at 46% of flooding. The variation of effluent concentrations with gas and liquid flow rates are shown in

Table 1. Flooding Velocity vs. Concentration of Ammonia, Total Carbon Dioxide and Total Organic Carbon for Omega-9 Retort Water for a 2.07 m (6.8 ft) Column Height and a Liquid Rate of 2485 kg/h-m^2 (509 lb/h-ft^2) of Column Cross Section.

Liquid Rate (kg/h-m^2)	Gas Rate (kg/h-m^2)	Flooding Velocity (%)	NH_3 (mg/L) Before	NH_3 (mg/L) After	Total CO_2 (mg/L) Before	Total CO_2 (mg/L) After	TOC (mg/L) Before	TOC (mg/L) After	Stripping Temperature (°C)	Column Pressure kPa
2485	1899	46	3983	1549	8006	4309	840	---	82.2	161
2485	2646	65	3983	1311	8006	4024	840	680	82.2	193
2485	3584	88	3983	1310	8006	3803	840	670	82.2	217
2485	1899	46	3983	57	8006	2394	840	---	93.3	161
2485	2646	65	3983	51	8006	1905	840	450	93.3	193
2485	3584	88	3983	0	8006	1808	840	440	93.3	217
2485	1899	46	3983	0	8006	1759	840	---	104.4	161
2485	2646	65	3983	0	8006	1771	840	430	104.4	193
2485	3584	88	3983	0	8006	1686	840	430	104.4	217

Figures 5 through 8 for ammonia and carbon dioxide. For the flooding range investigated in this work, the gas flow rate had little effect on the amount stripped from the retort water, particularly at the higher stripping temperatures. Since the stripping process exhibits a much greater dependence on the liquid flow rate, the liquid phase resistance can be assumed to be rate controlling. As the ammonia carbonates decompose at the higher temperature a larger amount of free ammonia and carbon dioxide will become available in the retort water for stripping. Thus, as found in this study, the effects of liquid flow rate will become smaller at higher temperatures.

Stripping curves that relate effluent concentrations to column height are given in Figures 9, 10, and 11 for Run 17 retort water. Although the carbon dioxide concentration could be reduced to 291 mg/L at 104.4°C (220°F), the ammonia concentration in the effluent could not be reduced below 916 mg/L. However, the stripped water was heated to 110°C (230°F) and recycled through the column where it was stripped a second time. The ammonia and carbon dioxide concentrations were then reduced to 636 mg/L and 285 mg/L respectively. Effluent concentrations of ammonia and carbon dioxide are related to stripping temperature in Figures 12 and 13. If the amount of ammonia in the retort water is to be reduced to levels of low toxicity, the stripping temperature must be increased to approximately 121.1°C (250°F). This is about 2.8°C (5°F) below the boiling point of the water at the column pressure of 215 kPa (31.2 psia) used in this study. The column height must also be increased to about 457 cm (15 ft) as indicated by the results obtained after recycling the already stripped retort water. The effects of gas and liquid flow rates on the stripping process are shown in Figures 14 through 16. The rate of gas flow had little influence on the amounts of ammonia and carbon dioxide removed from the retort water. Again mass transfer and chemical reaction in the liquid phase controls the desorption process. A summary of the stripping results is given in Table 2 for the various flooding velocities.

Occidental Oil Shale Corporation's retort water, OXY-6, was the third water studied in this

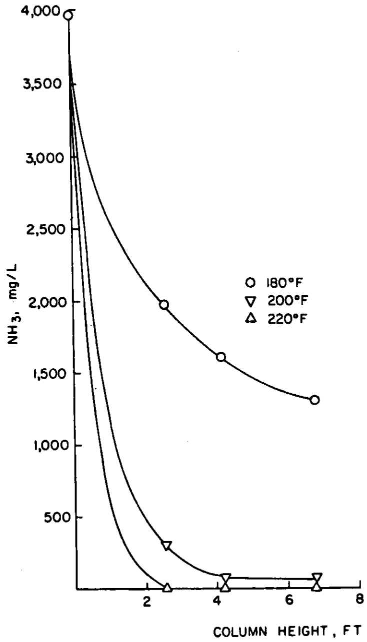

FIGURE 2. Omega-9 Retort Water Effluent Concentrations of NH_3 as a Function of Column Height and Stripping Temperature for a 2485 kg/h-m^2 (509 lb/h-ft^2) Liquid Rate and 2646 kg/h-m^2 (542 lb-h-ft^2) Gas Rate.

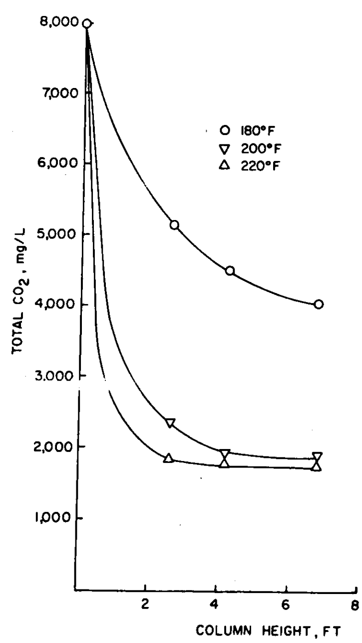

FIGURE 3. Omega-9 Retort Water Effluent Concentrations of Total CO_2 as a Function of Column Height and Stripping Temperature for a 2485 kg/h-m^2 (509 lb/h-ft^2) Liquid Rate and 2646 kg/h-m^2 (542 lb/h-ft^2) Gas Rate.

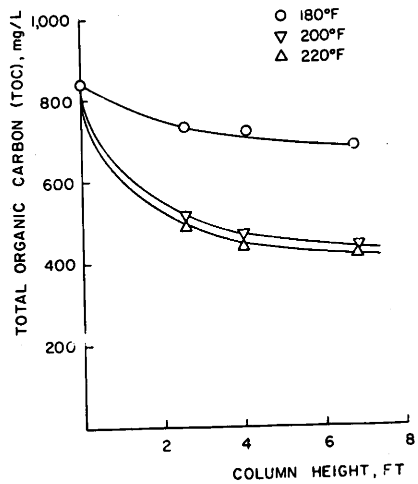

FIGURE 4. Omega-9 Retort Water Effluent Concentrations of TOC as a Function of Column Height and Stripping Temperature for a 2485 kg/h-m^2 (509 lb/h-ft^2) Liquid Rate and 2646 kg/h-m^2 (542 lb/h-ft^2) Gas Rate.

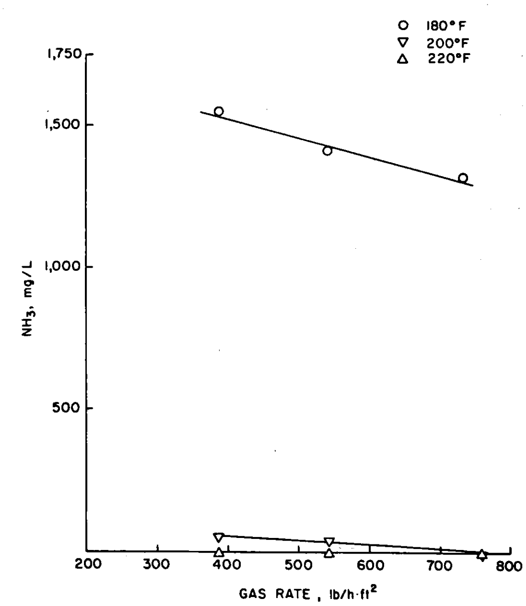

FIGURE 5. Omega-9 Retort Water Effluent Concentrations of NH_3 as a Function of Gas Rate and Stripping Temperature for a 2485 kg/h-m^2 (509 lb/h-ft^2) Liquid Rate and 2.07 m (6.8 ft) Column Height.

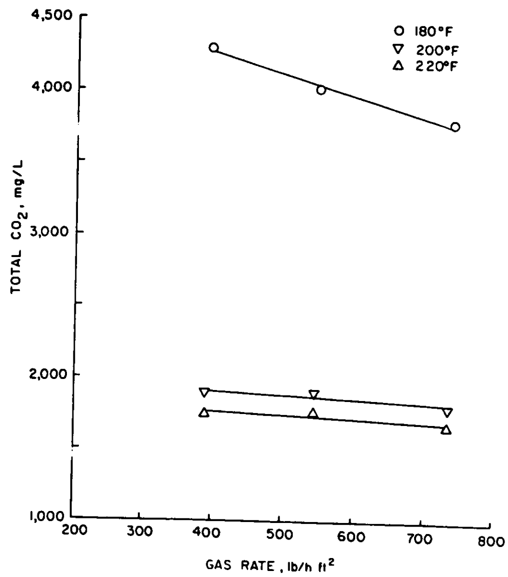

FIGURE 6. Omega-9 Retort Water Effluent Concentrations of Total CO_2 as a Function of Gas Rate and Stripping Temperature for a 2485 kg/h-m^2 (509 lb/h-ft^2) Liquid Rate and 2.07 m (6.8 ft) Column Height.

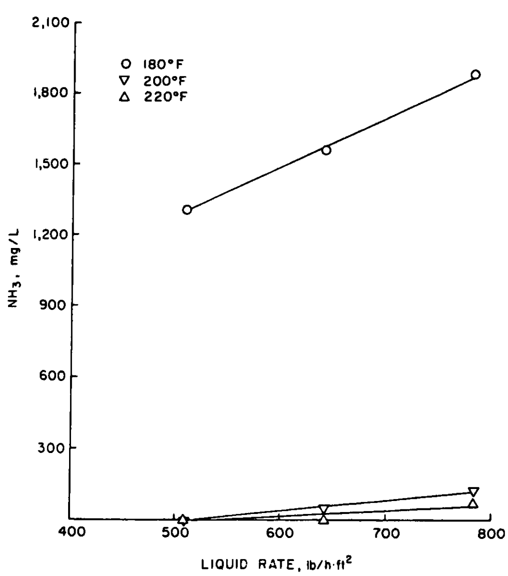

FIGURE 7. Omega-9 Retort Water Effluent Concentrations of NH_3 as a Function of Liquid Rate and Stripping Temperature for a 2646 kg/h-m^2 (542 lb/h-ft^2) Gas Rate and 2.07 m (6.8 ft) Column Height.

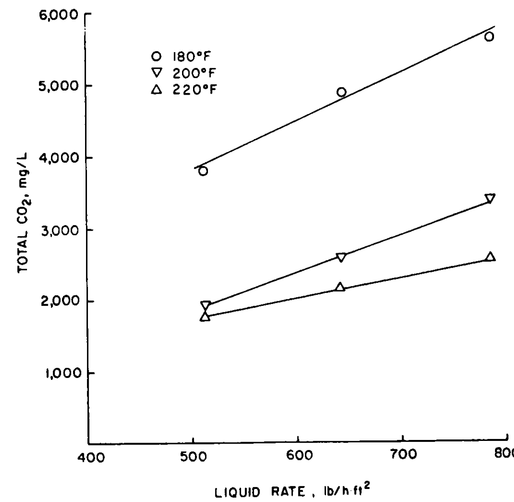

FIGURE 8. Omega-9 Retort Water Effluent Concentrations of Total CO_2 as a Function of Liquid Rate and Stripping Temperature for a 2646 kg/h-m^2 (542 lb/h-ft^2) Gas Rate and 2.07 m (6.8 ft) Column Height.

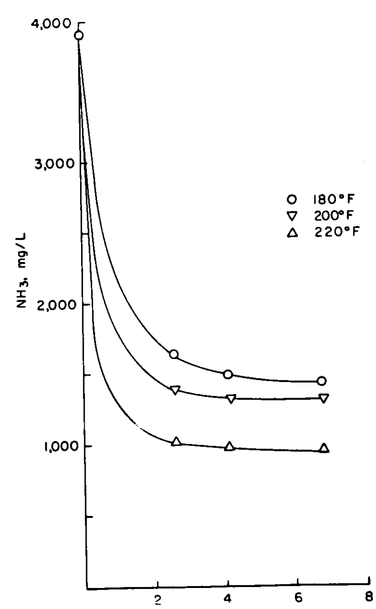

FIGURE 9. Run-17 Retort Water Effluent Concentrations of NH_3 as a Function of Column Height and Stripping Temperature for an 1802 kg/h-m^2 (369 lb/h-ft^2) Liquid Rate and 2490 kg/h-m^2 (510 lb/h-ft^2) Gas Rate.

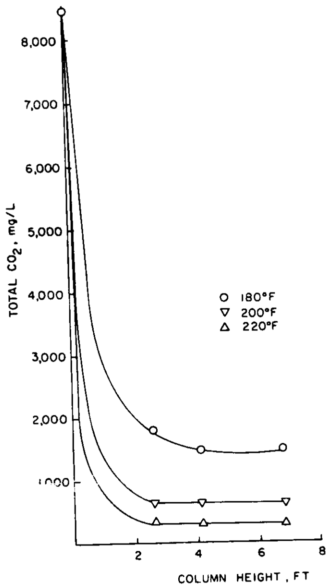

FIGURE 10. Run-17 Retort Water Effluent Concentrations of Total CO_2 as a Function of Column Height and Stripping Temperature for an 1802 kg/h-m^2 (369 lb/h-ft^2) Liquid Rate and 2490 kg/h-m^2 (510 lb-h-ft^2) Gas Rate.

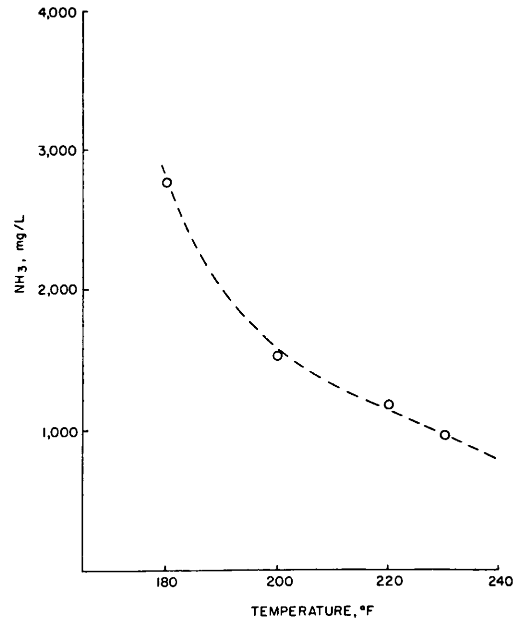

FIGURE 12. Run-17 Retort Water Effluent Concentrations of NH_3 as a Function of Column temperature for a Column Height of 2.07 n (6.8 ft) 1802 kg/h-m^2 (369 lb/h-ft^2) Liquid Rate, and 3584 kg/h-m^2 (734 lb/h-ft^2) Gas Rate or 87% Flooding Velocity.

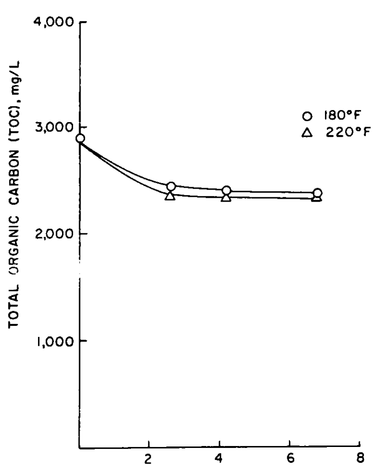

FIGURE 11. Run-17 Retort Water Effluent Concentrations of TOC as a Function of Column Height and Stripping Temperature for an 1802 kg/h-m^2 (369 lb/h-ft^2) Liquid Rate and 2490 kg/h-m^2 (510 lb-h-ft^2) Gas Rate.

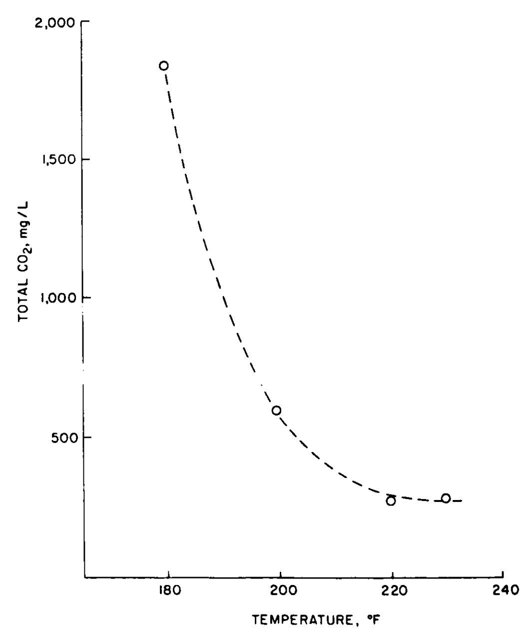

FIGURE 13. Run-17 Retort Water Effluent Concentrations of Total CO_2 as a Function of Column Temperature for a Column Height of 2.07 m (6.8 ft), 1802 kg/h-m^2 (369 lb/h-ft^2) Liquid Rate, and 3584 kg/h-ft^2 (734 lb/h-ft^2) Gas Rate or 87% Flooding Velocity.

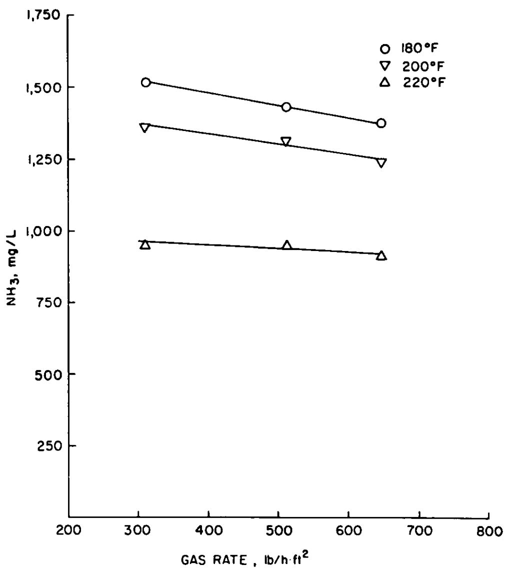

FIGURE 14. Run-17 Retort Water Effluent Concentrations of NH_3 as a Function of Gas Rate and Stripping Temperature for a Column Height of 2.07 m (6.8 ft) and an 1802 kg/h-m^2 (369 lb/h-ft^2) Liquid Rate.

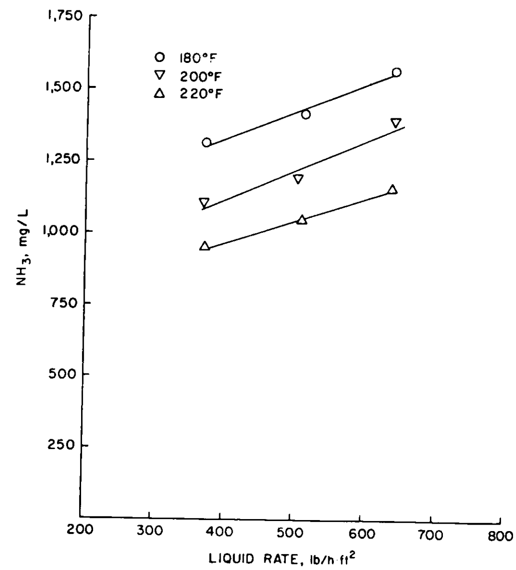

FIGURE 16. Run-17 Retort Water Effluent Concentrations of NH_3 as a Function of Liquid Rate and Stripping Temperature for a Column Height of 2.07 m (6.8 ft) and a 2490 kg/h-m^2 (510 lb/h-ft^2) Gas Rate.

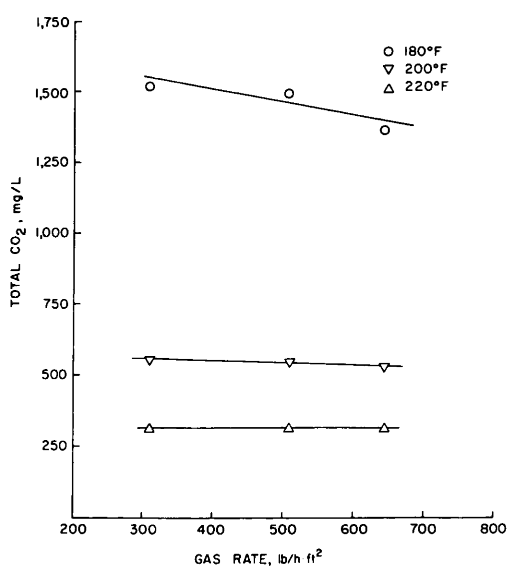

FIGURE 15. Run-17 Retort Water Effluent Concentrations of Total CO_2 as a Function of Gas Rate and Stripping Temperature for a Column Height of 2.07 m (6.8 ft) and an 1802 kg/h-m^2 (369 lb/h-ft^2) Liquid Rate.

project. The effluent concentrations of ammonia, carbon dioxide, and TOC are related to column height in Figures 17 through 19 for stripping temperatures of 82.2 and 104.4°C (180°F and 220°F). The ammonia concentration was reduced to less than 50 ppm for a stripping temperature of 104.4°C (220°F) and a column height of 2.07 m (6.8 ft). This result was achieved at a flooding velocity of 48.6% as shown in the summary presented in Table 3. As noted in this table, the gas flow rate had little influence on the stripping effectiveness. The influence of liquid flow rate on the amount of ammonia removal is shown in Figure 20. As found for the other retort waters, the liquid flow rate has a significant effect on the stripping process.

Table 2. Flooding Velocity vs. Concentration of Ammonia, Total Carbon Dioxide, and Total Organic Carbon for Run-17 Retort Water for a 2.07 m (6.8 ft) Column Height and a Liquid Rate of 1802 kg/h-m^2 (369 lb/h-ft^2) of Column Cross Section.

Liquid Rate (kg/h-m^2)	Gas Rate (kg/h-m^2)	Flooding Velocity (%)	NH_3 (mg/L) Before	NH_3 (mg/L) After	Total CO_2 (mg/L) Before	Total CO_2 (mg/L) After	TOC (mg/L) Before	TOC (mg/L) After	Stripping Temperature (°C)	Column Pressure kPa
1802	1514	35.2	3915	1515	8464	1517	2880	2480	82.2	159
1802	2490	61.0	3915	1447	8464	1495	2880	2340	82.2	193
1802	3139	76.9	3915	1378	8646	1341	2880	2330	82.2	219
1802	1514	35.2	3915	1362	8464	616	2880	---	93.3	159
1802	2490	61.0	3915	1345	8464	615	2880	---	93.3	193
1802	3139	76.9	3915	1311	8464	550	2880	---	93.3	219
1802	1514	35.2	3915	952	8464	311	2880	2340	104.4	159
1802	2490	61.0	3915	946	8464	309	2880	2320	104.4	193
1802	3139	76.9	3915	916	8464	291	2880	2320	104.4	219

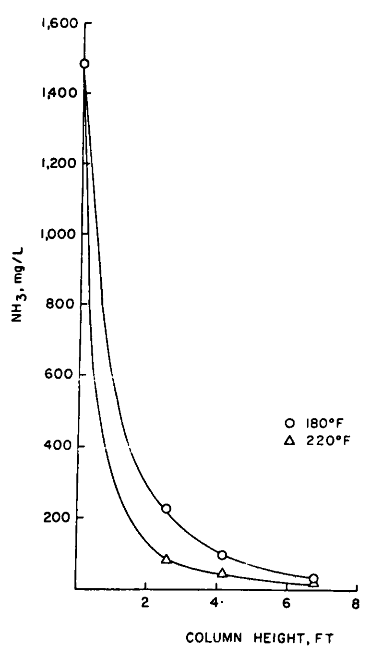

FIGURE 17. OXY-6 Retort Water Effluent Concentration of NH_3 as a Function of Column Height and Stripping Temperature for an 1802 kg/h-m^2 (369 lb/h-ft^2) Liquid Rate and 1929 kg/h-m^2 (395 lb-h-ft^2) Gas Rate.

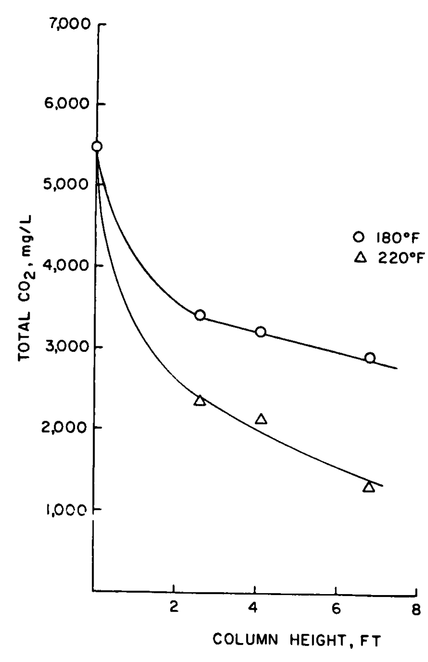

FIGURE 18. OXY-6 Retort Water Effluent Concentrations of Total CO_2 as a Function of Column Height and Stripping Temperature for an 1802 kg/h-m^2 (369 lb/h-ft^2) Liquid Rate and 1929 kg/h-m^2 (395 lb/h-ft^2) Gas Rate.

Table 3. Flooding Velocity vs. Concentration of Ammonia, Total Carbon Dioxide, and Total Organic Carbon for Run-17 Retort Water for a 2.07 m (6.8 ft) Column Height and a Liquid Rate of 1802 kg/h-m^2 (369 lb/h-ft^2) of Column Cross Section.

Liquid Rate (kg/h-m^2)	Gas Rate (kg/h-m^2)	Flooding Velocity (%)	NH_3 (mg/L) Before	NH_3 (mg/L) After	Total CO_2 (mg/L) Before	Total CO_2 (mg/L) After	TOC (mg/L) Before	TOC (mg/L) After	Stripping Temperature (°C)	Column Pressure kPa
1802	1269	32.9	1481	55	5457	2894	2500	---	82.2	159
1802	1929	48.6	1481	45	5457	2785	2500	---	82.2	193
1802	1269	32.9	1481	41	5457	1275	2500	1670	104.4	159
1802	1929	48.6	1481	10	5457	1187	2500	1550	104.4	193

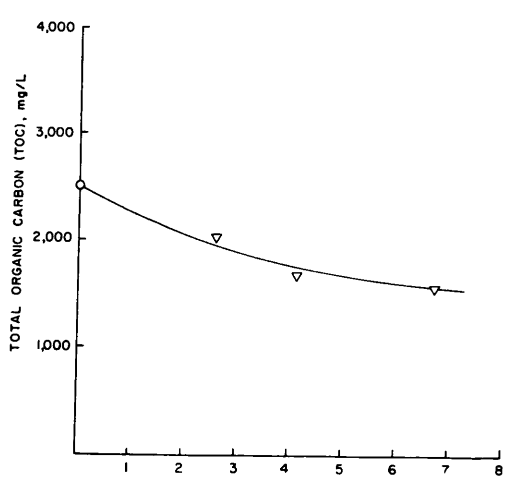

FIGURE 19. OXY-6 Retort Water Effluent Concentration of TOC as a Function of Column Height and Stripping Temperature for an 1802 kg/h-m^2 (369 lb/h-ft^2) Liquid Rate and 1929 kg/h-m^2 (395 lb-h-ft^2) Gas Rate.

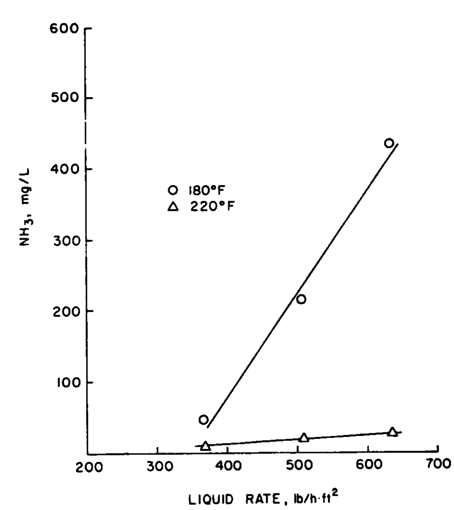

FIGURE 20. OXY-6 Retort Water Effluent Concentration of NH_3 as a Function of Liquid Rate and Stripping Temperature for a Column Height of 2.07 m (6.8 ft) and a 1929 kg/h-m^2 (395 lb/h-ft^2) Gas Rate.

CONCLUSIONS

This project demonstrates that both ammonia and carbon dioxide can be removed from solution for the Omega-9 and OXY-6 retort waters at the stripping temperatures and flow conditions used in this study. Although hot gas stripping reduced the ammonia and carbon dioxide in Run-17 retort water, the stripping process is less effective for this type water at the stripping temperatures employed. It was demonstrated, however, that the ammonia could be reduced to lower levels by increasing the stripping temperature and column height. High stripping temperatures and low liquid flow rates resulted in lower ammonia and carbon dioxide concentrations as expected. The results showed that the rate of stripping was controlled by the liquid phase. The design of a stripping column to treat retort waters should be significantly taller than the 2.07 cm (6.8 ft) column used in this study in order to accommodate the variations found in the different waters. A stripping temperature only slightly less than the boiling point of the retort water is recommended.

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