

A TRANSPORTABLE STEAM STRIPPER FOR THE
PILOT SCALE TREATMENT OF OIL SHALE
WASTEWATERS: DESIGN, FIELD TESTING,
AND CHEMICAL ANALYSIS

John R. Wallace
William J. Culbertson
Charles H. Habenicht
Michael Shaffron

Charles H. Prien Center for Synthetic Fuel Studies
Denver Research Institute
University of Denver
Denver, Colorado

ABSTRACT

In September, 1980, a pilot-scale steam stripper was field tested in conjunction with the operation of the 150 ton Simulated In Situ Retort located at the Laramie Energy Technology Center. During operation of the retort, the steam stripper was integrated with the remaining pollution control equipment, including a venturi scrubber and thermal oxidizer, and significant interactions were observed. This test, the first field operation of the DRI transportable steam stripper, also provided useful information on system mechanical and operational stability. This information is now being incorporated into a redesigned system which will include more reliable measurement equipment and automatic controls.

The methods of chemical analysis required for the operation of the steam stripper are also discussed including, in particular, methods for determination of sulfide and total dissolved solutes. It is important to note that levels of sulfide up to 450 mg/l were observed in the wastewater from the venturi scrubber, although these concentrations rapidly decayed even in filtered and refrigerated samples. The latter result may explain why sulfide has not usually been found in wastewater from direct mode retorts and cautions against the determination of sulfur species on stored samples.

INTRODUCTION

Steam stripping has been proposed by several groups as part of an integrated water treatment system for oil shale wastewaters. In such integrated plans the steam stripper would remove the volatile gases such as ammonia, hydrogen sulfide, and light

organic compounds, thereby rendering the waters more amenable to reverse osmosis, biological degradation, or disposal on the spent oil shale pile.

Essentially, steam stripping is a partial distillation which is accomplished on an industrial scale by passing water counter-current to steam in a packed column. The objective is to remove the maximum amount of undesirable dissolved gases with a minimum amount of water. In laboratory tests this procedure has worked well. For example Hicks (1980) was able to remove 90% of the organic material and essentially 100% of the ammonia from an Oxy condensate water using this procedure. Murphy (1979) used hot air stripping on a variety of retort waters and reported essentially 100% removal of carbon dioxide and ammonia.

However, to the best of my knowledge, steam stripping has not been tested on a pilot scale using fresh retort water simultaneously with the retorting process. This factor is particularly important because of the known instability of retort waters. Of course, pilot scale tests also must be made in order to scale the process to a commercial size, a requirement for its realistic economic analysis.

For these reasons the Denver Research Institute has constructed and field tested a transportable steam stripper designed to treat approximately ten gallons per minute. Although the overall objective of this test is to understand under what conditions the volatile gases can be successfully stripped from retort water, several lesser objectives also were important. The first consideration was the mechanical and pneumatic stability of the stripper system and attached controls, including factors such as the reliability of the pumps, the achievement of steady flows at the desired temperatures and pressures, and the general ruggedness of the plumbing system. The second objective was to evaluate the reliability of the pressure, temperature, and flow rate meters as well as the data logging system. Third, we wished to obtain scale up information to assist in the design of a commercial scale stripper. A fourth objective was to determine the inter-

action of the steam stripper with the other pollution control systems and with the oil shale retort. A final objective was to determine which methods of sampling and chemical analysis were most appropriate and reliable under field conditions.

The field test discussed in this paper was completed during September 8-18, 1980 in conjunction with the operation of the 150 ton Simulated In Situ Retort located at the Laramie Energy Technology Center. The pilot scale steam stripper treated and returned wastewater produced by a venturi scrubber which was being tested as a means of controlling particulate matter in retort gas. The overhead vapors from the steam stripper were sent to a thermal oxidizer where they were combusted along with the retort gas from the 150 ton retort. The analytical methods tested during this run included conductivity, pH, ammonia, total dissolved solids, total inorganic carbon, and total organic carbon in wastewater. In addition, a prototype system for measuring total sulfur in retort gas was field tested.

This paper first describes the steam stripper and the results obtained during the September field test. These results largely relate to the mechanical and monitoring aspects of the steam stripper, although the efficiency of stripping will also be described. Based on results of the field test the stripper is being redesigned significantly and these modifications will be described. Finally, I will discuss briefly our development and field testing of analytical methods for the gases and waters involved.

PHYSICAL DESCRIPTION AND FIELD OPERATION

The steam stripping system used during the original field tests is shown in somewhat simplified form in Figure 1. As can be seen, the system consists of heat exchangers to warm the intake water to a temperature at or near its boiling point followed by a packed column. In the column, which is approximately 1 ft. in diameter by 8 ft. long and packed with Berl saddles, water flows downward counter-current to the upward flow of steam. This high temperature, countercurrent system was designed to remove dissolved gases-- NH_3 , H_2S , CO_2 , and light organic compounds--from the water within the packed column zone. These compounds exit the column with the steam through a vent at the top of the column. A portion of the overhead steam is then condensed and the remaining overhead vapors are sent to the

thermal oxidizer for incineration. Stripped water was pumped to storage and periodically recycled to feed the venturi scrubber.

During operation temperatures were measured using thermocouples at six locations throughout the system. Pressures were monitored using piezoelectric sensors at five locations throughout the system, and flow rates were measured using rotameters for liquid flows and an elbow tap for the inlet steam rate.

The first part of the field operation tested the thermal and mechanical integrity of the steam stripper including the ability to measure and balance flow rates and to achieve temperatures in the required range. Perhaps more important this stage also revealed interactions between the various systems--retort, scrubber, stripper, and thermal oxidizer--which were not apparent until all systems were operating simultaneously. Such interactions thus suggest in microcosm the interactions which would be expected during full scale retorting.

During integrated operation of the retort, thermal oxidizer, scrubber, and stripper several problems as well as their solutions became apparent. These will be discussed by considering first the interactions between the various systems, and then the mechanical performance of the isolated stripper.

One of the problems first apparent was the difficulty of balancing the flow rates of the scrubber and stripper. When the scrubber was operated at the lower flow rates, the stripper could operate only by recirculating part of the stripped water, a wasteful procedure. In practice this problem could be solved by proper scaling of the stripper and scrubber. Additional water storage could also permit either the stripper or scrubber to operate independently so that an outage of one system would not necessarily stop the other.

Another important consideration was interaction between the thermal oxidizer and overhead vapors. Pressure at the thermal oxidizer often prevented or made difficult the exhaust of overhead vapors. Also, surges of steam or condensate in the overhead vapor line occasionally extinguished the thermal oxidizer. For

the flow diagram shown in Figure 1 this problem could be relieved by pumping the overhead vapors under sufficient pressure to assure a constant flow rate, or at least by operating the stripper at a pressure significantly higher than the thermal oxidizer. Of course, in actual practice the exhaust from a steam stripper would not go to a thermal oxidizer, but more likely would go to a sulfur recovery system such as a Stretford unit. Nevertheless, the pressure created by whatever device is placed downstream from a steam stripper in a commercial retort will present a finite back pressure which in turn could affect the operation of the stripper.

During extended operation of both the scrubber and the stripper the water became hotter than desirable for ideal scrubbing performance. This can be remedied by the addition of a water cooling system, a solution which in fact was partially achieved in the field with an air cooled radiator.

With the steam stripper, the major problem was achieving sufficiently high temperatures in the column. The first limitation was that certain PVC components of the plumbing system, which appeared adequate on the drawing board, were inadequate in practice. This limitation was overcome in the field by replacing such parts with steel components. In future work, better temperature control can be achieved by adding heat exchanger capacity, by providing for additional steam injection, and by pressurizing the column.

Although flows were balanced throughout the system, flow monitors were less than ideal because of plugging and leaking problems. The piezo-electric pressures sensors, although attractive on paper, required excessive maintenance.

Manual data logging was also a time-consuming chore and of questionable value when operating parameters were changing rapidly and the plant required full time operator attention. These problems can be solved through the use of different monitors as well as automatic data logging.

In perspective it is important to note that the mechanical, pneumatic and monitoring aspects of the trailer operated successfully both as isolated systems and in conjunction with the scrubber and thermal oxidizer. As is expected with any system there were minor problems during the start of operation as discussed in the previous

paragraphs. Modifications in design and construction of the steam stripper are now underway and will be discussed later in this report.

Another important result of the field test is the experience gained in integration of multiple pollution control systems. This experience can be summarized by saying that better buffering is required between the various systems so that a failure in one does not disrupt the others. That is, a failure of the stripper should not disrupt the scrubber operation. This principle will apply to a greater degree as the oil shale retorting plants become more complex, and is equally important regardless of the type of control equipment eventually selected.

RESULTS

During operation of the stripper, water samples were collected periodically in order to determine the efficiency of removal of the various gases. The inlet sample was collected immediately after the inlet surge tank shown in Figure 1 and the outlet sample was collected immediately before the outlet surge tank also shown in Figure 1. The removal efficiency was then calculated by comparing the inlet and outlet concentrations and assuming that the influent and effluent flow rates were equal.

Once the mechanical and pneumatic problems were solved, the stripper column was operated in the temperature range of 210 to 216°F. During this time the stripper clearly removed significant amounts of dissolved gases as is shown in Table 1. This table is based on the average results for 11 pairs of samples. Although not included in this table, pH was also measured and increased an average 0.4 pH units during passage through the column, indicating that the acid gases were removed slightly more effectively than ammonia. It is encouraging also that the decrease in electrical conductivity, which is a crude measure of total dissolved material, is on the same order as the other components.

In conclusion, the steam stripper, as operated in this test, can effectively remove

(or at least decompose) H₂S and to a lesser degree NH₃, CO₂, and some organic components. The removal of the latter components is significantly less than has been achieved in the laboratory where removal efficiencies close to 100% have been observed. This disappointing removal efficiency may be due to several possibilities including the presence of other ions which would "fix" the ammonia or CO₂, or the occurrence of channeling or foaming in the column. At this time the diagnostic tools are not available for distinguishing among these various explanations although such measurements are being included in future tests.

Table 1
REMOVAL OF VOLATILE GASES BY STEAM STRIPPING

Species	Influent Concentration Range	Average Removal Efficiency %
Electrical conductivity (m mhos cm ⁻¹)	2.7-4.8	68
NH ₃ + NH ₄ (mg/l as N)	320-1600	54
Sulfide (mg/l)	200-450	>95
Total Inorganic Carbon (mg/l as C)	240-470	57
Total Organic Carbon (mg/l as C)	260-410	63

MODIFICATIONS

At the present time the DRI steam stripper is being significantly modified to incorporate our findings during the first field test. One of the major goals is to incorporate automatic fluid controls and data logging so as to relieve the operator of these chores. At the present time automatic temperature and pressure transducers are being installed to permit almost continuous monitoring of these parameters.

The pneumatic system, shown in Figure 2, is also being changed significantly. Most noticeable is the reflux condenser added to the overhead vapors in order to more efficiently separate the volatile gases from the water. As shown in the diagram a pressure regulated valve is added to the overhead gases in order to make the pressure in the stripper column more independent of the downstream pressures. The influent and effluent water streams will be set by a continuously modulated

level sensor in control of a triplex piston pump. In addition, heat exchangers are being upgraded so as to more efficiently heat the influent water stream.

ANALYTICAL METHODS

During the field test analyses were completed in a mobile laboratory located at the test site in order to provide rapid feedback to the operators. This arrangement also allowed us to observe fresh samples, which is an important consideration for some of the labile species found in retort waters.

A more detailed description of the analytical methods is found in the references by Habenicht et al. (1980) and Wallace (1980). Described here are only features of most interest to a general oil shale community audience.

In order to minimize degradation, samples were cooled immediately after collection and filtered through a 0.45 micrometer membrane filter under pressure. Although this is the recommended method for preserving retort waters, it was not adequate for these samples. In addition, this procedure was cumbersome and time-consuming, especially when the filters became plugged (as they often did), and is not well suited for field operation. Therefore, in future field operations this step should be avoided whenever possible.

Electrical conductivity and pH were determined by the standard electrode and conductivity cell. It is important to realize that the pH and electrical conductivity of the samples in this study varied in a manner more complex than normally observed in strong electrolytes. For this reason samples had to be equilibrated to 18 to 25°C before measuring these parameters, and this requirement likely applies to other retort wastewaters as well. It is important to note that for retort waters the temperature adjustments included in many pH and conductivity meters are not adequate for correcting these measurements to room temperature.

Ammonia was measured using the ammonia ion selective electrode. Although acceptable reproducibility and recovery was obtained

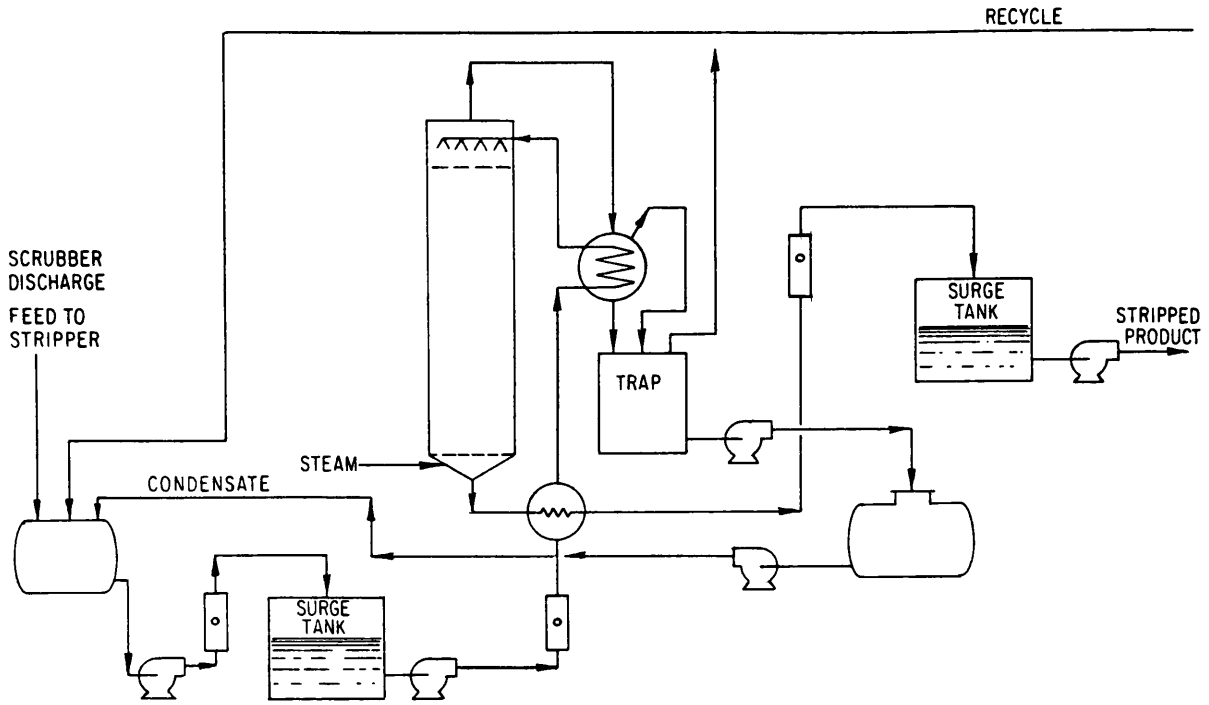


Figure 1. FIELD TESTED STEAM STRIPPER

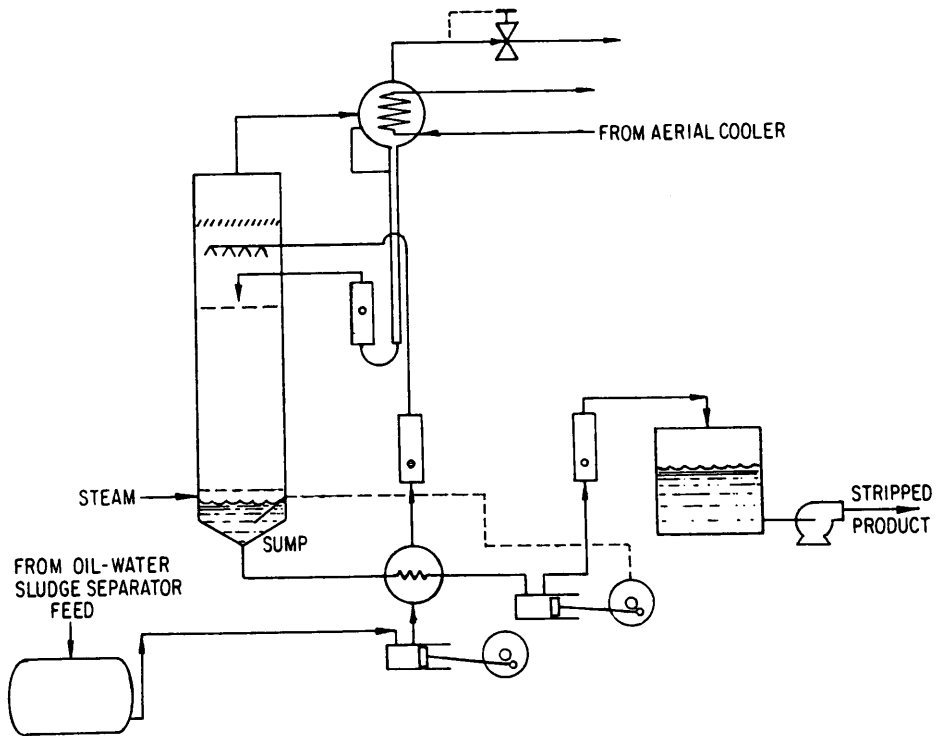


Figure 2. MODIFIED STEAM STRIPPER

using this technique, drifting response was nevertheless a problem. For this reason, the operator had to spend an unreasonable amount of time recalibrating the electrode and changing the electrode membrane, making this method more time-consuming than desirable for a field worthy procedure.

Total organic carbon (TOC) and total inorganic carbon (TIC) were measured on a Beckman model 915A total Organic Carbon Analyzer, which is based on the infrared detection of evolved CO_2 . It is important to realize that the more commonly employed titrimetric method for CO_2 is inappropriate for retort wastewaters containing high levels of ammonia and organic acids.

Sulfide was measured by titration with lead nitrate using a silver sulfide electrode as an end point indicator. A more thorough discussion of this technique, including sampling interferences, range of applicability, precision, and accuracy is found in a separate report, "The Analysis of Oil Shale Waste Waters for Sulfide," being prepared under EPA contract 68-03-2791, or in monthly progress reports for the same contract. In summary this procedure is applicable to retort wastewaters containing more than one mg/l of sulfide. It is free from interference due to chloride, thiocyanate, sulfate, thiosulfate, carbonate, ammonia and turbidity. Analyses, as performed under field conditions, are reproducible to plus or minus 3%.

The most important finding with regard to sulfide is its rapid disappearance. Even when samples are filtered and stored at 4°C , sulfide essentially disappears within two weeks and initially disappeared at a rate of approximately 20% per day. Thus if analysis had been performed after a shipment to a permanent laboratory, erroneous results would have been obtained. The presence of a field laboratory in this study was essential to obtaining meaningful analyses.

To the author's knowledge this study is the first to report major amounts of sulfide in wastewater from a direct mode retort. Quite possibly previous studies have missed sulfide because of its rapid disappearance during storage. It is noteworthy that previous studies have reported thiosulfate, sulfate, and thiocyanate as the major forms of sulfur in such retort waters. However,

based on our studies such species may arise due to the oxidation of sulfide and may not represent the original forms of sulfur.

The presence of sulfide in retort waters may be important in the design of water treatment systems because sulfide, unlike most higher oxidation states of sulfur, can be removed by steam stripping while sulfur in other forms cannot.

Subsequent to the field test in September we have developed additional techniques for analyzing oil shale wastes. One of these tests, which measures the total solute content of wastewater, can be considered as a replacement for the total dissolved solids (TDS) test which is widely used by wastewater engineers.

As is well known, the standard TDS test, which is actually the residue left when a water sample is evaporated to dryness, is not applicable to oil shale wastewater due to the evaporation of major quantities of NH_3 , CO_2 , and other volatile components. In addition, the TDS measurement is too slow to use under normal field conditions. A test which did not require drying of the sample would clearly be preferable. Total solute content is also measured by several colligative properties such as boiling point elevation and osmotic pressure.

After considering several colligative properties of water, we have selected the freezing point depression as the colligative property most indicative of total solute content for oil shale wastewaters. Table 2 illustrates the application of this technique to simulated and actual retort waters. The ideal osmolality would be the total molar strength for all the ions and neutral molecules in solution if the freezing point depression were exactly linear with molality. The measured osmolality is the freezing point depression in $^\circ\text{C}$ divided by 1.86°C , the freezing point depression per mole at infinite dilution. As can be seen, the measured osmolality is sufficiently close to the actual molal strength for most field applications. The final column in Table 2 shows the concentration of NaCl giving the same freezing

point depression as the actual solution. Comparing the second and fourth columns in this table shows that the freezing point depression gives an indication of total solute content, including ions, neutral inorganic species, and organic species, up to a 3 molal concentration within an accuracy of 7%. This procedure can also be performed automatically using devices available from most supply houses, making it an ideal tool for the plant operator who needs a rapid and convenient indicator of gross changes within his process.

Wastes: A Review. Denver Research Institute.
EPA Contract #68-03-2791.

Table 2

TOTAL SOLUTE BY FREEZING POINT DEPRESSION

<u>Sample</u>	<u>Ideal Osmolality</u>	<u>Measured Osmolality</u>	<u>NaCl Equivalent</u>
1.0 M NH_4HCO_3 + 0.1 M NH_4OH	2.1	1.81	2.0
0.1 M NH_4HCO_3 + 0.01 M NH_4OH	0.21	0.216	0.21
0.01 M NH_4HCO_3 + 0.001 M NH_4OH	0.021	0.021	0.021
1.0 M NH_4HCO_3 + 0.1 M NH_4OH + 0.921 M. Acetone	3.02	2.64	2.8
W-9 Retort Water	-	0.58	

REFERENCES

- Habenicht, C. H., Jovanovich, A., Shaffron, M., Wallace, J., Hicks, E. and Liang, L. 1980. Treatment of Oil Shale Wastewaters: Report of Field Test. DRI Report #5-31343.
- Hicks, E. 1980. Personal communication, Water Purification Associates.
- Murphy, C. L. 1979. Hot Gas Stripping of Ammonia and Carbon Dioxide from Simulated and In Situ Retort Waters. Ph.D. Thesis, Colorado School of Mines.
- Wallace, J. R. 1980. The Analysis of Oil Shale