

THE UTILIZATION OF RESIDUAL HEAT
IN SPENT MIS RETORTS FOR
WASTEWATER TREATMENT AND PROCESS IMPROVEMENTS

Dr. Norman E. Hester
Occidental Research Corp.
P.O. Box 19601
Irvine, California 92713

Carl Jacobson
Occidental Oil Shale, Inc.
P.O. Box 2687
Grand Junction, Colorado 81502

ABSTRACT

At the end of a normal retorting period, a spent MIS retort contains in excess of 100 gigajoules (100 billion BTU) of residual heat in the form of hot retorted shale. Experiments conducted at the close of retorting operations for Occidental's Retorts 7 and 8 show that much of the residual energy can be used for water purification and/or recovered as products of the water-gas reaction of steam with residual char.

INTRODUCTION

Oil shale in the western United States offers the potential of being a major source of domestic liquid fuels. In order to exploit the vast reserve of oil shale, Occidental Petroleum has developed the modified-in-situ (MIS) retorting technology to produce a crude oil from kerogen-containing rocks. The Occidental MIS process has been discussed in detail in a number of publications,¹⁻³ and basically consists of mining a void in an area of rich shale, fracturing the shale with explosives, and then igniting the rock in place (in-situ) to pyrolyze the kerogen in front of an advancing flame front. At the end of the normal retorting procedure, a spent MIS retort contains almost 3.5×10^8 Kg of (8×10^8 lb) of spent shale at temperatures ranging from 260°C (500°F) to in excess of 815°C (1500°F). This translates into over 100 gigajoules (10^9 BTU) of residual heat.

In a commercial operation when hundreds of retorts are allowed to transfer their heat to the surrounding support pillars in the mine, the temperature of the pillars could be raised to a sufficiently high level that mechanical strength would be lost. Subsidence could then occur. On the other hand, this residual heat presents the opportunity to improve the overall

process efficiency if the energy can be removed and put to good use. Experiments designated to recover this heat have been conducted at Occidental Research Corporation on a pilot plant scale and at the close of operations of commercial sized Retorts 7 and 8. These experiments were designed to test the efficiency of using water for heat removal from the retort and to gather data on the quantity and usefulness of the products generated.

EXPERIMENTAL

Quenching studies on full sized retorts were done at the close of operations of Retorts 7 and 8 at Logan Wash, CO. Detailed information concerning the descriptions and operations of these retorts is being presented by other authors at this symposium.^{4,5} After oil production has fallen off from hundreds of barrels per day to a few barrels per day, retorting was considered complete. The quenching of Retorts 7 and 8 began on November 9 and November 19, 1982, respectively. Retort 8 was quenched by addition of water through the surface wellheads. Retort 7 was quenched by injection of water through holes drilled into the retort at an upslant from the air level and above the original rubble surface. The plan for quench was to maintain a water flow of 50 gal/min (140 l/min) into each retort and this was accomplished for Retort 8. However, a shortage of water on site forced us to reduce the flow into Retort 7 to about 0.06 m³/min (15 gal/min) after 3 weeks. After 4 days the flow into Retort 7 was cut off completely for one week, and then brought up to 0.01 m³/min (10 gal/min) for 42 days. Water addition to Retort 7 ceased on Feb. 8, 1983.

Data acquisition continued throughout the quench for many of the same parameters as were measured during retorting. Temperatures in the

retort, gas temperatures and flows; gas composition, oil and water products were all followed as described in another paper.⁵ Additional water samples were taken to characterize in some detail the chemical species in the water being used for the quench, the water collected at the bottoms of the retorts, and the condensed steam.

RESULTS AND DISCUSSION

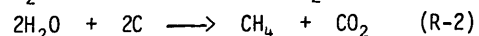
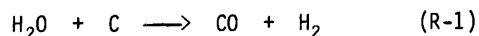
The data analyses for this study are divided into four areas; gas production and composition, water balance and water quality information, energy balance and fuel calculations. The quality of the data varies depending on the stream and quantity being measured. In general liquid flow rates and dry gas compositions are more accurate than wet flows and humidities. The most important data for these studies were the compositions, stack flow rates and surface condensate flows. This information when combined with individual retort flow measurements and isokinetic sampling data made it possible to analyze each retort.

Because of the rather inconsistent operation of Retort 7, our data analysis will focus on Retort 8 with much lesser data reported for 7.

Gas Production and Composition

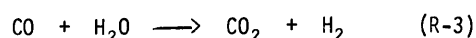
The composition of the off gas on a dry basis for Retort 8 is shown in Figures 1 and 2 for H₂, N₂, CH₄, CO and CO₂. Water content of the off gas is a nominal 80%. The plots cover a time period of approximately 6 weeks before the quench started (water addition started Nov. 9) through the end of February. The quench operation was still going on at the time of preparation of this paper.

The sharp increase in hydrogen and methane production at the start of water addition is indicative of the reaction of steam and carbon, with the carbon being in the form of residual char in the retorted shale. The major reactions of water with char are:

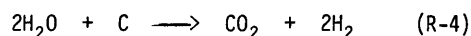


If water is present in excess and temperatures high enough, CO can react with another water

as follows:



The rate in Figure 2 shows a rapid decrease in CO concentration when water was added. This indicated that reaction R-3 is very rapid and that the net reaction (R-1) + (R-3) better represents the chemistry:



The compositional data in Figures 1 and 2 show some interesting trends for N₂ and CO₂. N₂ levels show an increasing trend with time. Since we were not intentionally adding air to the retorts, we must assume that the retorts had developed additional leaks during this period. However, during the same period CO₂ concentrations decreased. If the CO₂ levels were dominated by the presence of air in the retort i.e. O₂ + char → CO₂. Then CO₂ and N₂ should both increase. If CO₂ levels are dominated by the water-char reactions (R-2 and R-4), then CO₂ and H₂ should have similar trends. Since neither of the above seem to be true, we are led to assume that CO₂ production in the retort is (at least initially) dominated by carbonate decomposition which is still quite pronounced while the retort is hot but lessens with decreasing temperature. It is also probable that as the retort cools further, considerable CO₂ could be reabsorbed by residual metal oxides.

Gas production results for Retort 8 are summarized in Figures 3 - 5. Figure 3 shows the total dry gas production with time and Figures 3 and 4 show the production numbers for H₂, CO₂, CH₄ respectively. It is interesting to compare at this point the H₂ production in Retort 7 (Figure 6) with that of Retort 8 (Figure 4). Water addition into Retort 7 was 0.04 m³/min (10 gal/min) from Dec. 21 to Feb. 8 while the rate of addition to Retort 8 was 0.2 m³/min (50 gal/day) with water addition into 8 at a rate 5-times that into 7, it is seen that the rate of production of hydrogen from 8 is only twice that of Retort 7. There would seem to be an optimum rate of water addition into the retorts depending upon the goals. If one wishes to make the most hydrogen for a given amount of heat removal, then slow addition would be chosen. If one wishes to

Figure 1
Offgas Composition During Quench of Retort 8

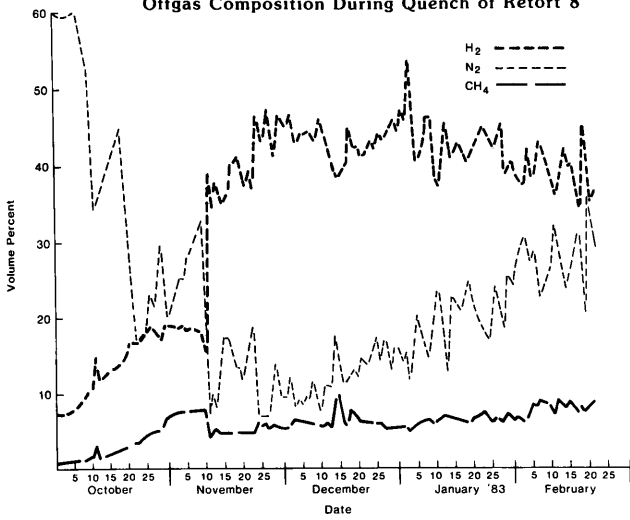


Figure 2
Offgas Composition During Quench of Retort 8

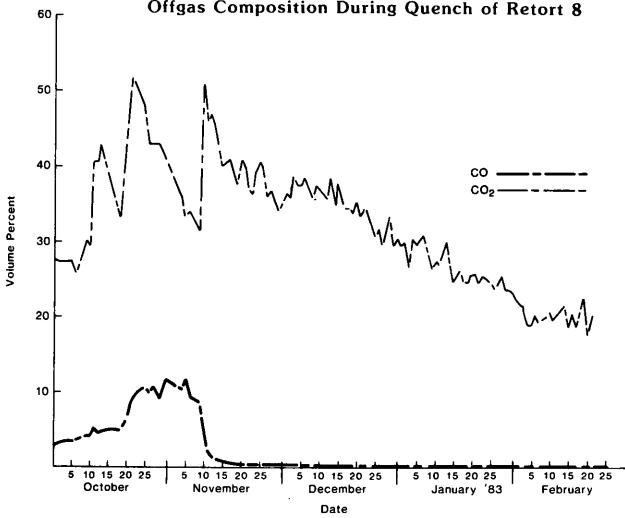


FIGURE 3
RETORT 8
DRY GAS PRODUCTION

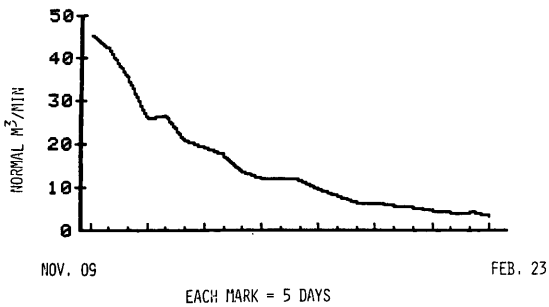


FIGURE 4
RETORT 8
H₂ AND CO₂ PRODUCTION

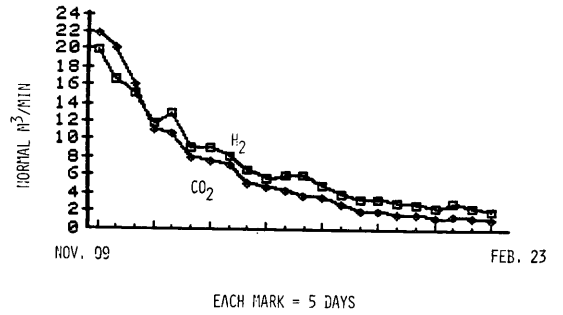


FIGURE 5
RETORT 8
CO AND CH₄ PRODUCTION

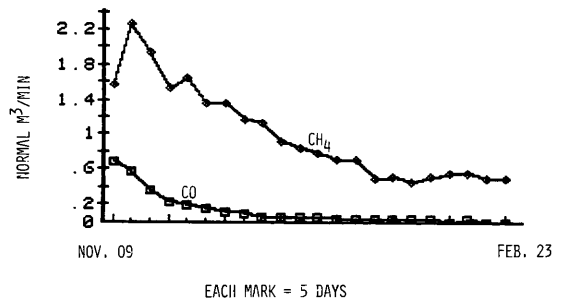
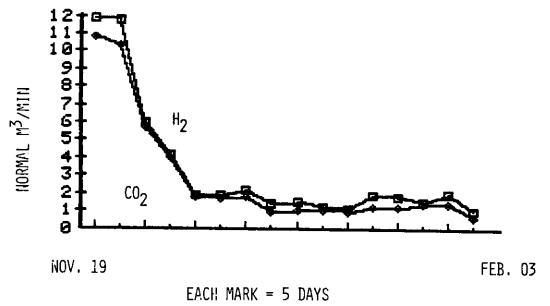


FIGURE 6
RETORT 7
H₂ AND CO₂ PRODUCTION



cool rapidly with minimum hydrogen formation, an increased rate of water addition would be chosen.

Water Balance and Water Quality

All liquid flows into and out of the retorts were measured with the exception of ground water influx. Retort 8's water influx was estimated to be $3 \times 10^{-3} \text{ M}^3/\text{mm}$ (0.9 gal/mm) based on data obtained in November, 1981 before retorting started.

The total water vapor from the retorts was a sum of the surface condensate and stack loss. The stack water loss was calculated assuming that the stack gas was saturated at the contact condenser exit temperature and pressure.

Figures 7 through 9 show the various production or consumption rates as a function of time.

Figure 7 plots the quench rate, that is the rate of water addition through the "air holes" in Retort 8. Water was added through 12 of the 16 holes with the 4 corner holes closed. Also shown in Figure 7 is the quantity of water pumped from the bottom of the retorts through the lower level bulkhead. This flow began to increase in January. It is believed that much of this increase can be attributed to the channeling of water down the sides and the walls of the retorts. In early March, (not indicated on the plots) the quench water flow was routed to only the four center holes in the retort and the bulkhead flows dropped to significantly lower levels.

Figure 8 shows plots of the amount of water being vaporized by the retort and the amount of water being produced by the retort. This later number is negative since the retort actually consumes water. The definitions for terms on the plots are:

$$\begin{aligned} \text{Water Vaporized} &= \text{water vapor out} \\ &\quad (\text{condensed \& uncondensed}) \\ &\quad - \text{water vapor in} \\ \text{Water Produced} &= \text{water vaporized} + \\ &\quad \text{bulkhead water} - \text{ground} \\ &\quad \text{water} - \text{quench water} - \\ &\quad \text{water entering to cool} \\ &\quad \text{lower bulkhead} = -(\text{water} \\ &\quad \text{consumed}) \end{aligned}$$

It is significant that over the time period covered by the plots (>100 days) that the amount of water vaporized has only dropped about 40%. It is realistic to assume that a significant amount of water could still be evaporated by the retort, and such an assumption is in essential agreement with conclusions drawn later when the energy balance is considered. The plot of the water produced in Figure 8 shows more water being consumed by the retort. This consumption is most likely due to water held up by hydration of cooled shale near the top of the retort.

Figure 9 shows the amount of water consumed by reaction with char. This plot is basically derived from the hydrogen and methane production rates assuming the chemistry described in equations (R-1), (R-2), and (R-3). The water consumed by these reactions was less than 10% of the total water consumed. Initially, these reactions consumed about $32 \text{ M}^3/\text{day}$, but this rate dropped rapidly to about $8 \text{ M}^3/\text{day}$ by early January.

It is clear from Figures 7 - 9 that most of the water entering the retort leaves as steam thus providing a type of distillation for the quench water entering from the top.

In this study, the quench water is a combination of the waters from the bottom of the retorts mixed with mine water and with water collected by the condenser. It would be expected that the waters going into the retort in a commercial operation would be the dirtiest available and similar to those collected at the bulkheads of Retorts 7 and 8.

Listed in Tables 1 and 2 are the analyses of the feed streams from Retorts 7 and 8 and the final quench water analyses. The "condenser" column of data represents the final analyses of the "purified water". Major metal ions such as boron, calcium, lithium, magnesium, potassium and sodium (represented in total by the TDS values) are removed quite well. Some of the anion species, chloride, fluoride, and sulfate; however, come on over. These species are associated with ammonium salts, which are quite volatile.

Those chemicals such as CO_2 (analyzed as total alkalinity, bicarbonate and carbonate)

FIGURE 7.-RETORT 8, WATER QUENCH RATE AND BULKHEAD FLOW

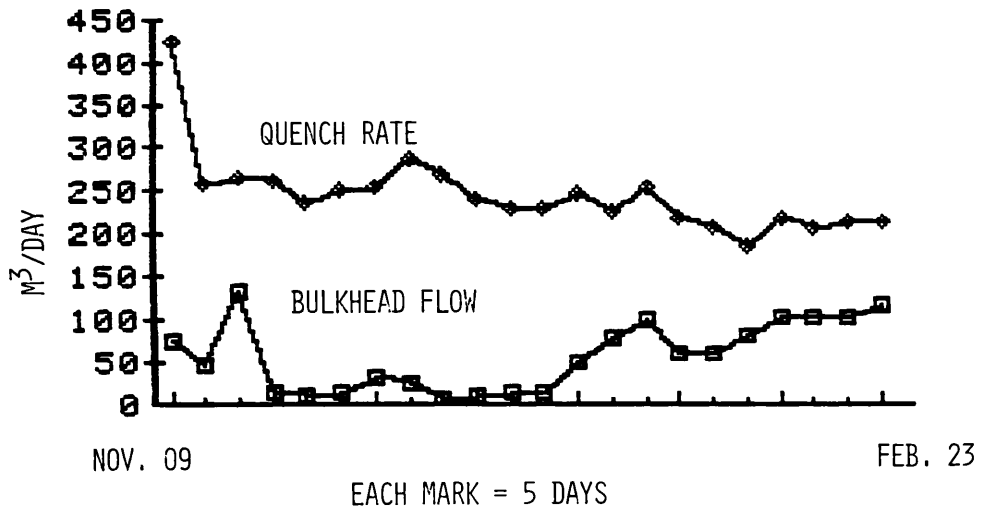


FIGURE 8.-RETORT 8, WATER VAPORIZED AND WATER PRODUCED

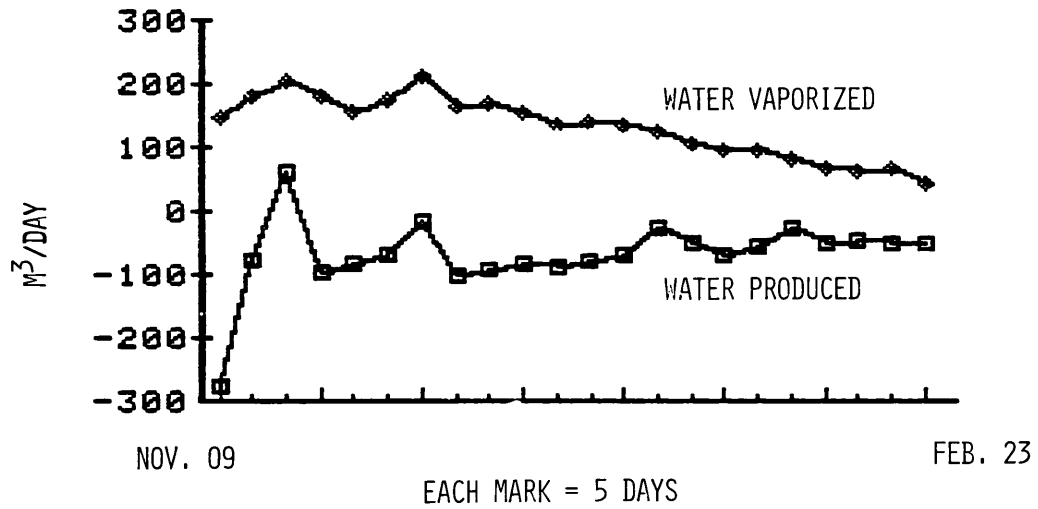
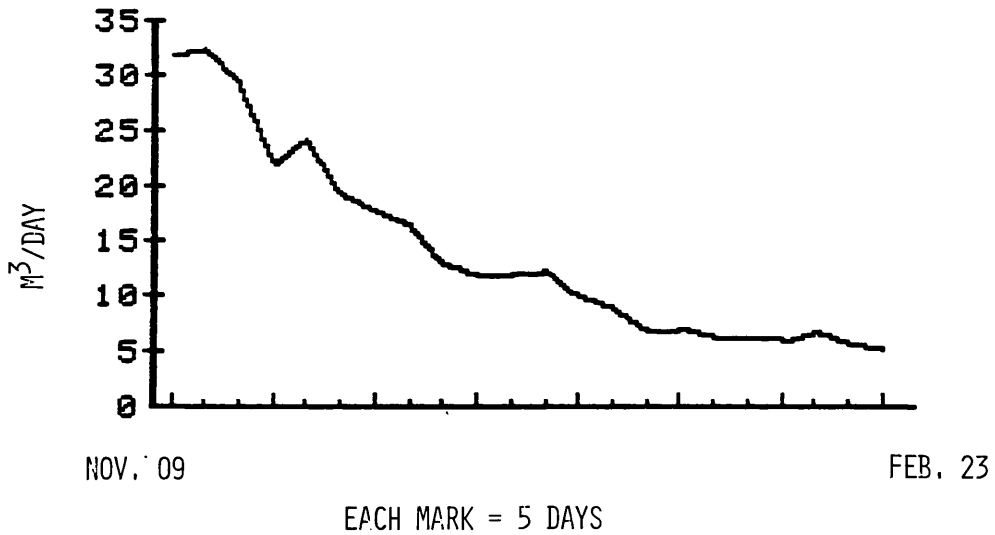


FIGURE 9.-WATER CONSUMED BY CHAR REACTIONS



QUENCH STUDY ANALYTICAL DATA
DECEMBER 7, 1982

TABLE 1

	RETORT 7	RETORT 8	QUENCH WATER	CONDENSER	PERCENT REMOVAL
ALUMINUM	<0.1 Mg/l	<0.1 Mg/l	<0.1 Mg/l	<0.1 Mg/l	-----
ARSENIC	1.8	1.3	0.2	0.04	80%
BARIUM	<0.5	<0.5	<0.5	<0.5	-----
BORON	54	58	8.2	<0.1	>98%
CALCIUM	1.4	40	2.2	0.8	64%
CHROMIUM	<0.02	0.02	<0.02	<0.02	-----
COPPER	<0.02	<0.02	<0.02	<0.02	-----
IRON	0.02	0.06	<0.02	<0.02	-----
LITHIUM	2.6	4.4	2.8	<0.05	>98%
MAGNESIUM	0.5	130	7.7	0.7	91%
MANGANESE	<0.02	0.02	<0.02	<0.02	-----
MERCURY	0.002	0.004	0.006	0.009	-----
MOLYBDENUM	0.02	<0.01	<0.01	<0.01	-----
NICKEL	0.06	0.08	0.02	<0.02	-----
POTASSIUM	1,500	1,300	150	3.2	98%
SELENIUM	<0.01	<0.01	<0.01	<0.01	-----
SODIUM	320	330	330	8.2	98%
ZINC	0.03	0.04	0.02	<0.02	-----
TOTAL ALKALINITY	2,700	1,400	18,000	23,000	-----
BICARBONATE	2,300	1,300	17,000	22,000	-----
CARBONATE	350	63	1,000	1,000	-----
CHLORIDE	640	590	2,900	2,800	3%
FLUORIDE	200	55	27	1.4	48%
AMMONIA	390	780	5,400	7,000	-----
KJELDAHL	400	800	9,400	7,000	-----
OIL & GREASE	140	190	39	32	18%
PHENOLS	5.4	13	2.7	2.3	15%
SILICA	120	23	14	<1	>92%
TOTAL DISSOLVED SOLIDS	1,000	15,000	1,500	71	95%
TSP	37	150	<10	<10	-----
SULFATE	2,300	6,100	400	2,000	-----
SULFITE	7	7	18.7	74	60%
THIOSULFATE	520	360	100	70	30%
THIOCYANATE	14	22	18	11	39%
TOTAL SULFUR	1,100	2,400	1,400	1,800	-----
DOC	930	2,200	440	380	14%
pH	9.4	9.1	8.9	8.8	

QUENCH STUDY ANALYTICAL DATA

DECEMBER 14, 1982

TABLE 2

	RETORT 7	RETORT 8	QUENCH WATER	CONDENSER	PERCENT REMOVAL
ALUMINUM	<0.1 Mg/l	<0.1 Mg/l	<0.1 Mg/l	<0.1 Mg/l	-----
ARSENIC	2.4	0.8	0.1	< 0.02	>80%
BARIUM	<0.5	<0.5	<0.5	< 0.5	-----
BORON	95	60	2.6	<0.1	>96%
CALCIUM	2.4	18	1.0	0.9	10%
CHROMIUM	<0.02	0.02	<0.02	<0.02	-----
COPPER	<0.02	<0.02	0.08	< 0.02	>75%
IRON	0.05	0.03	<0.02	< 0.02	-----
LITHIUM	3.0	2.3	0.07	<0.05	>28%
MAGNESIUM	1.2	110	1.9	0.5	74%
MANGANESE	0.02	0.03	<0.02	<0.02	-----
MERCURY	0.004	0.006	0.006	0.003	50%
MOLYBDENUM	0.05	0.1	<0.01	< 0.01	-----
NICKEL	0.08	0.08	0.04	< 0.02	>50%
POTASSIUM	1,800	760	25	0.6	98%
SELENIUM	<0.01	<0.01	<0.01	< 0.01	-----
SODIUM	4,400	2,900	97	4.1	96%
ZINC	0.06	0.03	<0.02	< 0.02	-----
TOTAL ALKALINITY	3,100	890	20,000	23,000	-----
BICARBONATE	2,600	850	17,000	21,000	-----
CARBONATE	500	40	3,000	2,000	-----
CHLORIDE	920	480	2,900	2,400	-----
FLUORIDE	260	54	5.4	1.5	72%
AMMONIA	1,200	780	7,000	7,400	-----
KJELDAHL	1,400	790	7,200	7,400	-----
OIL & GREASE	140	150	27	37	-----
PHENOLS	11	13	2.0	3.3	-----
SILICA	130	24	9.0	5.5	31%
TOTAL DISSOLVED SOLIDS	17,000	12,000	340	4.1	99%
TSP	52	150	< 10	< 10	-----
SULFATE	4,300	5,500	120	11	91%
SULFITE	17	6.0	120	48	60%
THIOSULFATE	680	130	190	140	26%
THIOCYANATE	19	16	21	1.8	91%
TOTAL SULFUR	1,800	1,800	1,400	1,300	6%
DOC	1,800	1,900	340	530	-----
pH	8.5	9.3	9.8	8.8	

and NH_3 continue to be high in the quench and condenser water, and in fact, are higher in the condenser water. High ammonia levels are consistent with the view that some retorting is still going on. The CO_2 is a product of retorting, the water-char reactions, and carbonate decomposition.

It is clear that this process greatly improves the water quality by removal of minerals. Experience by Monsanto⁶ with purification of condenser waters would lead us to believe that this water could be made into a very good quality industrial feed water with just steam stripping alone.

Energy Balance

Some of the most important information to be gained from the study is the rate and duration of cooling. Each spent retort contains about 110 gigajoules of energy at the start of quenching. It is a goal to reduce this to about 29 gigajoules in order to leave the retort with an average temperature of 120°C (250°F). Such temperatures in the retorts would leave little concern about thermal degradation of support pillars in the mine.

Quenching cools the retort in at least three ways; water vaporization, endothermic chemical reactions and the sensible heat lost to hot off gas and water. The cooling rate is plotted in Figure 10. Figure 11 shows the relative contribution to the cooling rate from the vaporization and reaction respectively.

The energy removed by vaporization was calculated by multiplying the vaporized water mass rate by the change in enthalpy. The cooling due to endothermic reactions was calculated from reaction enthalpies provided primarily by reactions R-1, R-2 and R-3. It can be argued that these reactions do not take place as simply as pictured by the equations. However, as long as the starting materials (water, char and air) produce the products H_2 , CO_2 , CH_4 and CO the estimate should be reasonably good. Our G.C. analyses indicate that our offgas also contains $\sim 4\% \text{C}_2^+$, the enthalpies from these reactions are also considered. The energy removed by hot bulkhead water and offgas was calculated by multiplying their mass flow rates by their corresponding changes in

enthalpy.

The biggest source of uncertainty in these estimates is due to the energy from retort water consumption. Most water consuming reactions such as lime slaking, and rehydrating spent shale should also be quite exothermic. However, we are missing data to quantify these reactions. For the purpose of these calculations, the water consumed by means of other than water/char reaction is assumed to be used for shale wetting. A nominal exothermic value of .55 Kcal/mole (1000 BTU/mole) was assigned as the heat of reaction. Figure 12 shows a plot of the sensible energy remaining in the retort. Over the 107 day period plotted, approximately 35 gigajoules of energy have been removed. Water vaporization accounts for approximately 84% of this cooling. Endothermic reactions removed 9% of the heat while 5% has left as hot off gases and water.

It should be noted that our overall cooling rate for the retorts is considerably less than was anticipated. This slower rate can in the most part be attributed to the fact that we have had a considerable amount of air leaking into the retorts (estimated from the nitrogen in Figure 1). The reaction of oxygen with char and/or hydrogen has introduced a considerable amount of heat back into the retort. Retorts 7 and 8 are quite different from our expected commercial operation retorts in that they have 16 downholes for air addition and hundreds of thermocouple holes. In short, we anticipate that our commercial retorts to be much less "leaky" to air. However, the fact that we have observed that the addition of air can extend the quench time is a good piece of information. If our overriding goal on a commercial operation is to cool the retorts as quickly as possible using the minimum amount of water, we will have to be quite careful to eliminate air leaks. On the other hand, if we have an extremely large amount of water to purify, we can extend the life time for distillation significantly by the deliberate addition of air during the quench operation.

Temperatures were followed in the retort during the course of the quench. Figures 13, 14 and 15 are the average temperatures with

FIGURE 10
RETORT 8
TOTAL COOLING RATE

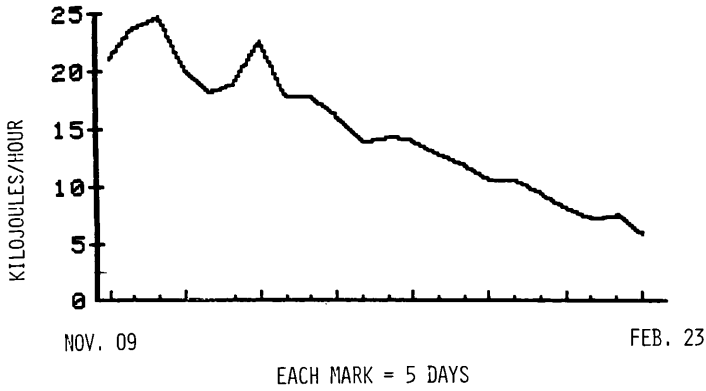


FIGURE 11
RETORT 8
ENERGY REMOVED BY
VAPORIZATION AND REACTIONS

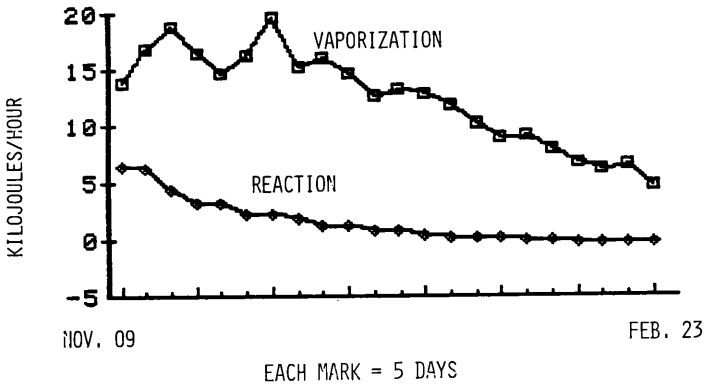


FIGURE 12
RETORT 8
REMAINING SENSIBLE ENERGY

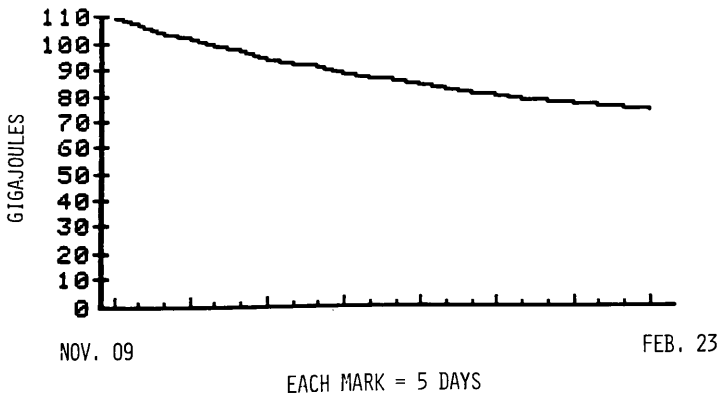


Figure 13
Retort 8
Average Temperature by Depth
Nov. 8, 1982

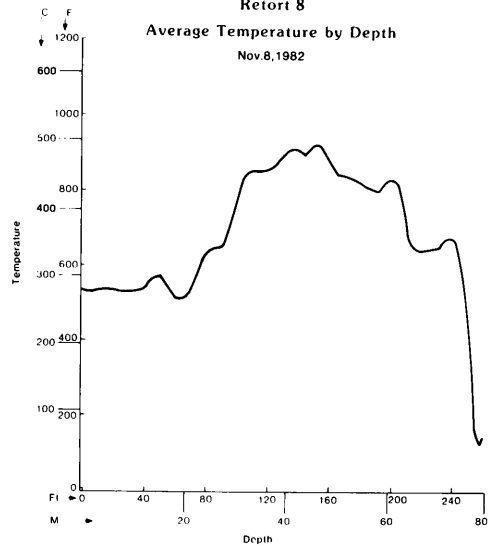


Figure 14
Retort 8
Average Temperature by Depth
Dec. 10, 1982

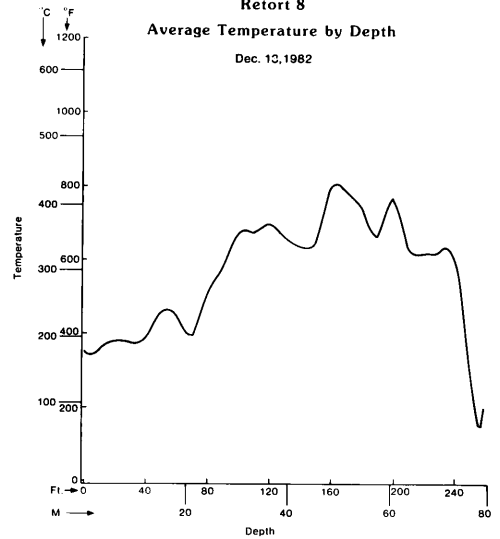
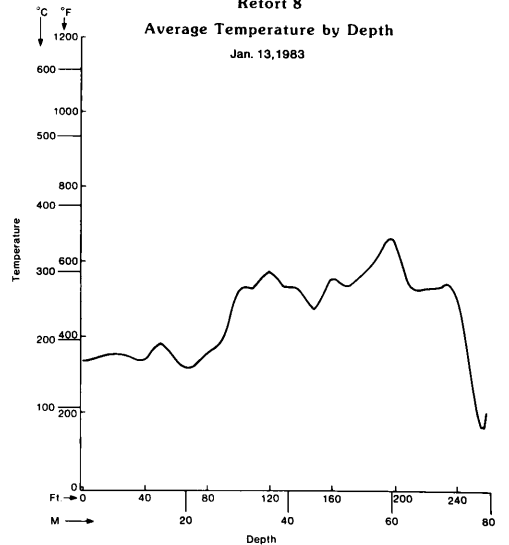


Figure 15
Retort 8
Average Temperature by Depth
Jan. 13, 1983



depth for Retort 8 on Nov. 8, the day before quench water was added, Dec. 13, and Jan. 13 respectively. The temperature plotted represents the averages of all thermocouples in vertical sections 3 meters (10 ft) thick. By the time the quench had started, approximately 80% of the initial thermocouples in the retort had been lost. Thermocouples were mounted on strings in the retort. If settling or burn destroyed a string at some point the thermocouple data from that point and inward toward the center of the retort was lost. The net effect is that the thermocouple data shown in Figures 13 - 15 tends to be dominated by data from close to the walls. Thus, the trends observed are a qualitative picture of what is happening in the retort but not quantitative.

Offgas Heating Value

The off gas heating values shown in Figure 16 were calculated using the compositions obtained from on-line gas chromatographs. Independent checks of these instruments⁵ revealed that they adequately detected the major components such as H₂, CO₂, CO, N₂ and CH₄ (shown in Figures 1 and 2) but normally understated C₂⁺ hydrocarbons. Therefore the data in Figures 16 and 17 are conservatively low. The dry gas net fuel energy plotted in Figure 17 is simply the dry gas heating values weighted by the total flow data (Figure 3).

CONCLUSIONS

1. Cooling of retorts by water quenching is a viable process. At a nominal water flow rate of 0.2 M³/min (50 gal/min), heat can be removed at a rate sufficient to cool a typical retort in a time period of from just a few months to one year with the time period dependent on how much air is allowed into the retort.
2. The quenching operation can be used as a means of converting high TDS process or retort water into a low TDS condensate.
3. The quenching operation produces an offgas rich in hydrogen and hydrocarbons. The offgas can be combusted for an energy source since it has a good heating value. Alternatively, since the hydrogen levels are high, this off gas could be used as a feedstock for oil upgrading.

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FIGURE 16
RETORT 8
DRY GAS NET HEATING VALUE

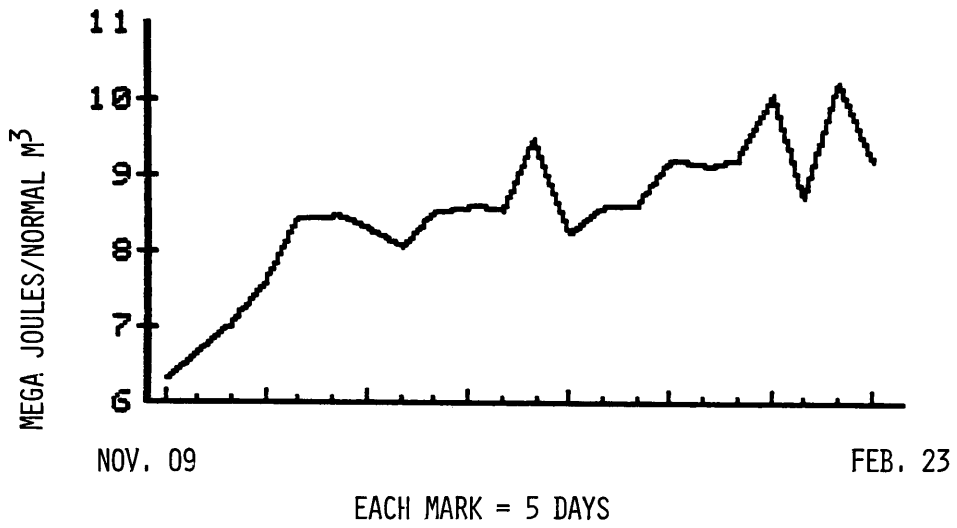


FIGURE 17
RETORT 8
DRY GAS NET FUEL ENERGY

