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**PREBURN VERSUS POSTBURN MINERALOGICAL
AND GEOCHEMICAL CHARACTERISTICS OF OVER-
BURDEN AND COAL AT THE HANNA, WYOMING
UNDERGROUND COAL GASIFICATION SITE**

By
Robert L. Oliver
Alv D. Youngberg

December 1983

Work Performed Under Contract No.: DE-AC07-76ET10723

For
U. S. Department of Energy
Office of Fossil Energy
Morgantown Energy Technology Center
Laramie Project Office
Laramie, Wyoming

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Robert L. Oliver¹ and Alv D. Youngberg²

ABSTRACT

Hundreds of mineralogic and geochemical tests were done under U.S. Department of Energy contracts on core samples taken from the Hanna underground coal gasification site. These tests included X-ray diffraction studies of minerals in coal ash, overburden rocks, and heat-altered rocks; X-ray fluorescence analyses of oxides in coal ash and heat-altered rocks; semi-quantitative spectrographic analyses of elements in coal, overburden, and heat-altered rocks; chemical analyses of elements and compounds in coal, overburden, and heat-altered rocks and ASTM proximate and ultimate analyses of coal and heat-altered coal. These data sets were grouped, averaged, and analyzed to provide preburn and postburn mineralogic and geochemical characteristics of rock units at the site. Where possible, the changes in characteristics from the preburn to the postburn state are related to underground coal gasification processes.

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INTRODUCTION

The Hanna Underground Coal Gasification (UCG) site is located in the SW $\frac{1}{4}$ of section 29 and the E $\frac{1}{2}$ SE $\frac{1}{4}$ of section 30 in Township 22 North, Range 81 West in Carbon County, Wyoming. Regionally, this is located in the coal-bearing Hanna Syncline of the Hanna Basin in south-east Wyoming. A number of underground coal gasification (UCG) experiments were conducted at the Hanna, Wyoming, Department of Energy site from 1973 to 1979 (Bartke, 1983). The individual experimental sites are referred to as Hanna I, Hanna II (Phases 1, 2, 3), Hanna III, and Hanna IV (a, b) (Figure 1).

Purpose and Scope

Several hundred pages of data done under U.S. Department of Energy contracts by several labs on the mineralogy and geochemistry of rocks at the Hanna site were available in various files and publications. Some data had been previously analyzed and evaluated, but much of the data was still in raw form on original lab sheets. One of the purposes of this report is to make this data available in a grouped and averaged format so other investigators can use the information without filtering through the massive data file. The other objective of this report is to present the mineralogic and geochemical characteristics of the preburn and postburn rocks at the site and document the changes evident. Some interpretation of these changes is also included and related to underground coal gasification processes in basic associations. The report is intended for usage by professionals of various disciplines involved in UCG studies to make more in-depth interpretations and analyses. The mineralogy section is mostly previously published data with new data on oxides and some additional interpretation. The geochemistry section is dominantly unpublished data with original interpretation.

Geologic Setting

The target coal bed of the Hanna UCG experiments was the Hanna No. 1 coal seam. This Tertiary coal seam was deposited in a poorly drained swamp in the flood plain of a fluvial system. It ranges in thickness from 25 to 32 feet and is overlain by 200 to 500 feet of overburden.

The overburden in this area consists of continental fluvial and lacustrine strata which may be divided into four broad lithologic units on the basis of sedimentary structures, grain size, texture, and depositional systems. These are referred to informally as Units A, B, C, and D, with A being the oldest (Craig et al., 1982) (Figure 2). For a detailed description of the Hanna site geology, see Oliver and Youngberg (1983).

Unit A is the overburden unit exhibiting the major control on cavity development of the UCG reactors. Unit A is found directly above the Hanna No. 1 coal seam and consists of siltstones and fine-grained sandstones with some claystones deposited in lacustrine delta and lacustrine environments. Its lateral continuity and thickness were

Figure 1. Location map of Hanna UCG experiments.

Figure 2. Subdivision of the overburden of the Hanna No. 1 coal bed at the Hanna UCG site (After Craig et al., 1982). * - Not present at Hanna UCG III; + - Not present at Hanna UCG II or Hanna UCG IV.

sufficient to confine all roof spalling to the unit. Therefore, only Unit A of the overburden will be treated in this paper.

MINERALOGY

Preburn

Overburden

The four basic rock types found in Unit A of the overburden at the Hanna UCG Site are: 1) sandstone; 2) siltstone; 3) mudstone; and 4) shale. These rock types and their relative abundance were calculated from core descriptions in Craig et al. (1982) on CH-131, CH-132, CH-133, and CH-134 and are shown in Figure 3. Sandstone comprises 48.9% of Unit A and it is a very fine- to fine-grained sublithic arenite which is often calcareous and contains some carbonaceous material. Siltstone makes up 35.8% of Unit A and it is often carbonaceous, 8.6% of Unit A consists of shale which is commonly carbonaceous, and mudstone with abundant carbonaceous material makes up 6.7% of the unit.

The bulk mineralogy of Unit A at the Hanna UCG site was determined in a study done by the Colorado School of Mines Research Institute (1979) and is shown in Figure 4. Quartz is the most common mineral, due to the dominance of the sandstone lithotype described above, comprising 53.1% of the unit mineralogy. It is more abundant than the other nine remaining minerals which include kaolinite, K-feldspar, dolomite, siderite, plagioclase, mica, calcite, and acmite+montmorillonite.

Grouping the minerals illustrated on Figure 4 shows that 18.0% of the unit mineralogy consists of carbonates (dolomite, siderite, and calcite). Aluminosilicates comprise 14.0% (K-feldspar and plagioclase), 8.9% is made up of clays (kaolinite and acmite+montmorillonite), and 6.0% micas.

Kaolinite, smectite, and illite are the clay mineral groups identified in overburden Unit A core samples. Kaolinite is the most abundant clay, followed by smectite and illite. A large percentage of the clay minerals present at the Hanna UCG site appear to have been transported into the site of deposition, although some clay minerals present do represent new crystallization (Craig, 1982.)

Coal

The mineralogy of the Hanna No. 1 coal was also determined in a study done by the Colorado School of Mines Research Institute (1979) and is shown in Figure 5. This chart illustrates the relative abundance of mineral constituents in the low temperature ash of the coal. As expected for a low energy sedimentary deposit, fine-grained clay minerals (kaolinite and illite) comprise nearly half of the coal ash. Quartz is the next most abundant mineral at 18.1%. This is just opposite of the pattern shown for Unit A of the overburden where quartz comprised over half of the mineral constituents and clay minerals only 8.9% (see

Figure 3. Overburden rock types in Unit A at the Ilanna UCG site. (Based on 304.5 feet of core from CH-131, CH-132, CH-133, and CH-134.)

Figure 4. Overburden bulk mineralogy in Unit A at the Hanna UCG site (Colorado School of Mines, 1979).

Minerals Identified in Hanna I Coal Bed (Low Temperature Ash)

Figure 5. Minerals in the Hanna No. 1 coal bed (low temperature ash), Hanna UCG site (Colorado School of Mines, 1973).

Figure 4). Twenty-two and six-tenths percent of the sample was unidentified or amorphous.

The distribution of calcium versus ash in the Hanna No. 1 coal of corehole CH-133 is shown in Figure 6. Note that the concentration of calcium is unrelated to ash percentage. Field observations support the hypothesis that calcite in the coal is a secondary fracture filling occurrence. (The importance of calcite cement in controlling spalling will be discussed in the section on diagenesis.) Sulfur distribution, however, is concentrated at the top of the coal as shown in Figure 7 and seems to be related to ash content. The direct relationships between ash percentage and element concentrations holds for all elements studied except calcium and possibly sodium, as can be seen by comparing the concentration profiles in the appendix.

The oxides comprising the ash of preburn Hanna bituminous coals were calculated from samples analyzed by Wyoming Analytical Laboratories, Laramie, Wyoming, using X-ray fluorescence and are shown in Table 1. The results were obtained by averaging 64 samples from coreholes CH-133, 2HP-170, and 2HP-171. The most abundant oxide in the ash is silicon dioxide with a mean level of nearly 47%. The least common occurring oxide is manganese oxide with a mean level of 0.11%. The highest single value is found for iron oxide (71.53%). The distribution and mineral forms of iron oxide in the coal bed from corehole I-16 is shown in Figure 8. The highest concentrations of iron oxide can be attributed to the presence of siderite bands.

Table 1. - Oxide analysis of ash in Hanna bituminous coals

Oxide	# Samples	High%	Low%	Mean%
SiO ₂	64	66.22	6.61	46.92
Al ₂ O ₃	64	28.25	3.32	22.49
Fe ₂ O ₃	64	71.53	3.01	10.30
CaO	64	21.95	0.34	7.23
SO ₃	64	12.66	0.29	4.80
MgO	64	5.87	1.49	2.43
Na ₂ O	64	2.92	0.84	1.33
K ₂ O	64	2.83	0.19	1.26
TiO ₂	64	1.99	0.13	0.84
P ₂ O ₅	64	6.15	0.01	0.78
MnO ₂	64	1.88	0.00	0.11

Figure 6. Distribution of calcium vs. ash in the Hanna No. 1 coal bed for Corehole CH-133, Hanna UCG site. (Samples analyzed by semi-quantitative spectrographic analysis, Spec. Resources, Inc.).

Figure 7. Distribution of sulfur in the Hanna No. 1 coa. for three coreholes, Hanna UCG site. (Samples analyzed by gravimetric method, Anwal Analytical and Consulting Laboratory).

Distribution of Iron Minerals and Iron in Coal Bed Core I-16

Figure 8. Distribution and mineral form of iron oxide in the Hanna No. 1 coal in Corehole 1-16, Hanna UCG site (Colorado School of Mines, 1979).

Overburden Diagenesis

The cement types found in the overburden sandstones are kaolinite, calcite, smectite, siderite, silica, chlorite, and pyrite. Kaolinite cement was present in almost all sandstone samples, where it occurred as a pore-filling cement. In some samples, calcite filled all the pores replacing feldspar grains and also the edges of quartz grains. In other samples, calcite occurred as single crystals, or small groups of crystals filling in the pore spaces. Siderite was found in sandstones containing significant amounts of clay matrix or clay clasts. Smectite was found sporadically distributed throughout the overburden as a pore lining, and silica was found scattered throughout the overburden in minor amounts. Pyrite and chlorite were found in very few samples and in minor concentrations. Where found, pyrite occurred as a noncrystalline mass surrounding detrital grains and chlorite occurred as isolated pore fillings (Craig, 1982).

The types and amount of cement in rocks immediately above UCG reactors appear to be significant variables in controlling the amount of roof collapse, since the cementing materials can control the strength of the overburden rocks. At the Hanna site, there appears to be a positive correlation between the amount of calcite cement present and the rock strength of the overburden. This positive correlation is suggested by a comparison of the Hanna II and the Hoe Creek III overburden rocks, as given in Ethridge et al. (1983). At the Hanna II Phases 2 and 3 site, only 42.6 ft. of overburden collapse occurred with no surface subsidence; while 127.9 ft. of overburden collapse with surface subsidence occurred at the Hoe Creek III UCG site. An important difference between the two sites is the amount of calcite cement contained in the overburden. At Hanna there was 10.8% calcite cement in the sandstones and siltstones compared to 0.2% calcite cement in the sandstones at Hoe Creek (Ethridge et al., 1983).

Postburn

Pyrometamorphic Rocks

The three pyrometamorphic rock types formed primarily from the overburden and found in the gasification cavities at the Hanna site are paralava rock (also called clinker, pseudolava, scoria, and slag), buchite, and paralava breccia. Paralava rock forms when melting of the original rock has taken place to such a degree that the material becomes mobile and the original sedimentary features can no longer be recognized. They are composed primarily of glass and euhedral high temperature mineral crystals. Paralava rocks also contain some mineral matter from oxidized coal. Buchites, as used in this report, are sedimentary rocks that have been partially melted and contain glass and high temperature minerals. Buchites have relict cross-bedding and other sedimentary structures preserved from the original rocks. Paralava breccia rocks consist of angular rock fragments that usually are pieces of buchite in a glassy or paralava rock matrix.

The mineralogy of the pyrometamorphic rocks from the Hanna II and Hanna III experimental sites was determined by petrographic and

X-ray studies (Burns et al., 1981, Ethridge et al, 1983, and Youngberg et al., 1983a and 1983b). Tables 2 and 3 list the minerals that were identified by these studies. Plagioclase (high temperature oligoclase) was the most common mineral formed during pyrometamorphism, with cordierite $[(\text{Fe,Mg})_2\text{Al}_4\text{Si}_5\text{O}_{18}]$ the next most common pyrometamorphic mineral formed. A monoclinic pyroxene, johannsenite $[\text{Ca}(\text{Fe,Mg,Mn})\text{Si}_2\text{O}_6]$, was identified in four samples and mullite $[3(\text{Al}_2\text{O}_3) \cdot 2(\text{SiO}_2)]$ was found in three samples. Two high temperature polymorphs of silica, cristobalite and tridymite, were fairly common in the pyrometamorphic rocks. Magnetite was present in all samples and relict alpha-quartz was found to be ubiquitous. Glass was a very common and often abundant constituent of the pyrometamorphic rocks. No clay minerals were found in any of the samples, even though these minerals were a common and often abundant constituent of the unaltered coal and overburden rocks. The temperatures attained during the period of pyrometamorphism must have been above the stability range for all clay minerals in the original rocks. Estimates of temperatures attained during gasification indicate a range of 1100°C to 1200°C (Youngberg et al., 1983a).

Figure 9 is a comparison of relative abundances of mineral groups in the preburn and postburn rocks at the site. This figure illustrates the dominance of silica over aluminosilicates and the abundance of clays and carbonates in the preburn rocks of Unit A and the Hanna No. 1 coal. Some mica, sulfates, and sulfides were also present. In the pyrometamorphic rocks, however, the aluminosilicates were as abundant as silica while the clays and carbonates disappeared. Some calcic-magnesium silicates were also present which were previously unseen in the unaltered rock.

The disappearance of the clays and carbonates noted for the pyrometamorphic rocks would indicate that these minerals are totally broken down during the pyrometamorphic process freeing up aluminum, magnesium, iron and calcium elements, respectively. Some silicate molecules must become available from the breakdown of clays and during the polymorphic change of quartz to cristobalite and tridymite as silicate molecules are free to bond with the available aluminum, magnesium, iron, and calcium to form the aluminosilicate and calcic-magnesian silicate minerals present in the pyrometamorphic rocks (oligoclase, cordierite, johannsenite, and mullite). The remaining silica converts to glass or is present as relict alpha-quartz. Some iron must have been available to bond with oxygen as indicated by the common occurrence of magnetite.

Coal Oxides

Core samples of preburn and postburn coals were analyzed for oxide content by Wyoming Analytical Laboratories, Inc., Laramie, Wyoming, using X-ray fluorescence. Table 4 is a comparison of preburn and postburn concentrations of oxides in the ash of the Hanna No. 1 coal. The preburn values were taken from Table 1. Values for char (heat-altered coal) were obtained by averaging concentrations for 25 samples from coreholes 2HP-172, 2HP-173, 2HP-174, and 2HP-176.

Table 2. - Mineralogy of pyrometamorphic core samples from
the Hanna II Phases 2 and 3 UCG site
 (After Ethridge et al., 1983)

Core Hole	2HP 181	2HP 181	2HP 181	2HP 181	2HP 181	2HP 181	2HP 181	2HP 172	2HP 172	2HP 176
Depth (ft)	259.1- 260.3	260.3- 260.8	260.8- 261.8	271.0- 271.8	278.9- 279.9	285.0- 286.0	289.2- 290.2	287.9- 288.9	288.9- 290.0	285.0
<u>MINERALS</u>										
Oligoclase high	-	-	-	X	X	-	X	X	X	X
Cordierite	-	-	-	X	X	X	X	X	-	X
Cristobalite (alpha)	-	-	-	X	X	X		X	X	-
Tridymite	X	X	X	-	-	-	-	X	-	-
Johannsenite	-	X	X	-	-	-	-	-	-	-
Mullite	-	-	-	-	-	-	-	X	X	-
Magnetite	X	X	X	X	X	X	X	X	X	X
Quartz (alpha)	X	X	X	X	X	X	X	-	-	-

Table 3. - Mineralogy of pyrometamorphic core samples from the
Hanna III and Hanna II Phase I UCG sites
(After Youngberg et al., 1983a and 1983b)

Hanna III Core	Depth (ft)	Oligo- clase	Cor- dierite	Cristo- balite	Try- dimite	Johann- senite	Mullite	Quartz	Glass
201	160.9	--	--	--	--	--	--	XX	XXX
204	171.5	--	--	--	--	--	--	XX	XXX
205	175.5	XXX	XX	XX	--	--	--	--	X
206	180.4	XXX	XX	XX	--	X	--	--	--

Hanna II
Phase I
Core

211	270.7	--	--	--	--	--	--	XXX	XXX
213	280.5	--	XXX	--	XXX	--	XXX	X	--
215	283.5	XXX	--	XX	--	--	--	X	--
216	283.5	XX	XX	XXX	--	--	--	--	X
219	284.5	XXX	--	XX	--	X	--	--	--

-- no peaks observed
X trace
XX moderate
XXX abundant

Figure 9. Preburn versus postburn mineral groups present in Hanna UCG rocks.

Table 4. - Oxides in ash of preburn and postburn coals, Hanna UCG site

Oxide	Preburn	Postburn	
	Coal (64)	Char (25)	Paralava (11)
SiO ₂	46.92	56.58	61.79
Al ₂ O ₃	22.49	22.74	20.88
Fe ₂ O ₃	10.30	8.15	6.76
CaO	7.23	4.45	2.92
SO ₃	4.80	1.81	0.46
MgO	2.43	2.12	1.68
Na ₂ O	1.33	0.96	0.95
K ₂ O	1.26	1.73	2.16
TiO ₂	0.84	0.77	0.76
P ₂ O ₅	0.78	0.31	0.18
MnO ₂	0.11	0.12	0.07

Remarks: Number of samples shown in parentheses.
Values reported in mean percent.

The average concentrations of oxides in paralava were determined from 11 samples taken from coreholes 2HP-172 and 2HP-176. Paralava rock has incorporated spalled fragments of Unit A and ash from the coal bed into the samples as it represents local melts of the original rock in the gasification cavity.

Examination of Table 4 illustrates rises in the levels of average concentration for SiO₂ and K₂O; decreases in levels of average concentration for Fe₂O₃, CaO, SO₃, P₂O₅, TiO₂, MgO, and Na₂O; and essentially unchanged levels for Al₂O₃ and MnO₂ (for the sequence: preburn coal to char to paralava). The progressive decrease in average concentration levels for Fe₂O₃, CaO, SO₃, TiO₂, MgO, Na₂O, and P₂O₅ may be interpreted as a release of these oxides into the gaseous or liquid effluents of the progressing gasification process. This is supported by the preceding discussion on postburn mineralogy. A rise in postburn concentrations of the related elements in the ground water at the experimental site would also be supportive of this hypothesis. Preliminary ground water analyses show a marked rise in postburn concentration levels for iron and sulfur species (Cooke and Oliver, in press). The apparent progressive increases in average concentration levels for SiO₂ and K₂O probably represent the concentrating effect of the release of other oxides into process effluents, and not an actual addition of silica and potassium to the postburn rocks.

GEOCHEMISTRY

Semi-Quantitative Spectrographic Analysis

Samples from cores taken at the Hanna UCG site were tested for Fe, Mg, Ca, Ti, Mn, Ag, B, Ba, Be, Co, Cr, Cu, La, Ni, Pb, Sc, V, Y, Zr, and Ga using the 6 Step D.C. Arc semi-quantitative spectrographic analysis technique. The analyses were done by Spec Resources, Inc., during 1981. These elements were selected to obtain a broad analysis of minor and trace elements present. One-hundred thirty-six samples from coreholes CH-131, CH-132, CH-133, and CH-134 were used to establish average preburn elemental concentrations for overburden Unit A. One-hundred fifty-three samples from coreholes CH-131, CH-132, CH-133, CH-134, 2HP-170, and 2HP-171 were used to establish average preburn elemental concentrations for the Hanna No. 1 coal. Twenty-one samples from coreholes 2HP-172, 2HP-173, 2HP-174, and 2HP-176 were used for calculating average elemental concentrations for postburn char (heat-altered coal). Eight samples from corehole 2HP-176 were used to determine average elemental concentrations for postburn paralava. The results are shown in Table 5.

Concentrations compared between preburn Unit A and preburn coal reveals that Unit A was higher than the coal in average concentrations for all elements studied. A comparison of values from Table 5 shows a trend of strong increases for all elements except Ag and Be from preburn coal to char to paralava, respectively. The increase in elemental concentrations from preburn coal to paralava is as much as tenfold (i.e. Ni and Zr). This represents the concentrating effect of burning off of carbon and in the paralava the inevitable mixing of rocks of higher average elemental concentrations from Unit A. A final comparison of preburn Unit A and paralava values shows that the average elemental concentrations of Fe, Ti, Ag, B, Ba, Be, Co, Cr, Cu, La, Ni, Pb, Sc, V, Y, and Zr are dominantly higher for paralava samples. Pyrometamorphic rocks in the cavity have attained even higher average elemental concentrations for these elements than those available from Unit A. This is probably due to the intense heat present in the gasification cavity. Mg, Ca, Mn, and Ga, however, show higher concentrations for preburn Unit A.

Minerals in the preburn rocks of Unit A and in the coal break down and supply free elements to the process effluents and to the local melts in the gasification cavity. Some of these elements bond to form new minerals in the pyrometamorphic rocks. Fragments of Unit A also spall into the cavity and mix with the melts. The elements supplied to the rocks in the gasification cavity from the breakdown of minerals in the coal and in fragments of Unit A which spall into the cavity and mix with the melts, plus the concentrating effect of carbon driven off through pyrolysis and oxidation, cause an increase in elemental concentrations in the char and paralava over preburn values of the coal and Unit A, respectively.

Table 5. - Preburn vs. postburn average concentration of 20 elements, Hanna UCG site

Unit (No. of samples)	(0.5) Fe%	(.02) Mg%	(.05) Ca%	(.002) Ti%	(10) Mn	(.5) Ag	(10) B	(20) Ba	(1) Be	(5) Co	(10) Cr	(5) Cu	(20) La	(5) Ni	(10) Pb	(5) Sc	(10) V	(10) Y	(10) Zr	(10) Ga
Preburn Unit A (136)	2.3	1.5	1.66	0.28	591	L(N)	57	832	1.4	11	59	22	46	26	27	13	84	31	248	110
Preburn coal (153)	0.8	0.4	0.28	0.09	96	*L(N)	*27	234	*L	*L(N)	*33	17	*L	*8	20	*5	53	*14	47	*L
Postburn char (21)	1.9	0.7	0.85	0.20	205	N	*34	463	1.7	*7	82	33	*49	17	27	12	94	34	99	*37
Postburn paralava (8)	5.3	1.0	1.59	0.55	394	N	81	938	1.5	22	144	36	73	63	37	23	174	53	313	55

Remarks: All values reported in ppm, unless otherwise specified
L - detected, but below detection limit (shown in parentheses)
N - not detected
N(L) - majority of data reported as N, some L values listed
L(N) - data listed about equally as L and N
* - both numerical and letter values listed in the data;
averages calculated by assigning N=0 and L= $\frac{1}{2}$ detection limit

Lithotype Analysis

The rock lithotype has a strong effect on minor and trace elemental concentrations in the geochemistry. Seven rock types are present at the site and will be analyzed in this section: 1) sandstone; 2) siltstone; 3) mudstone; 4) shale; 5) coal; 6) char; and 7) paralava. The overburden sections of Unit A in coreholes CH-131, CH-132, CH-133, and CH-134 were used to establish average elemental concentrations for sandstone, siltstone, mudstone, and shale, while the values used in Table 5 for the preburn Hanna No. 1 coal, postburn char and postburn paralava were used for coal, char, and paralava, respectively. The results are shown in Table 6.

An examination of Table 6 shows that the highest concentrations of an element are generally in paralava rock, although high relative elemental concentrations do occur in the shale lithotype. The highest average concentration of a given element is represented by one of these two rock types for all elements except Ca, Mn, Mg, and Be. Mudstone and siltstone, respectively, generally have middle range concentration values followed by char and sandstone. Coal has the lowest concentrations for all elements except Ag and Cu.

Among the overburden rock types, shale generally has the highest elemental concentrations followed by mudstone, siltstone, and sandstone, respectively. As the lithotype becomes more dominated by quartz, and clay minerals become less abundant, elemental concentrations decrease for most of the elements studied. An exception to this trend is the element Ca. The order of relative element concentration is reversed as Ca is present predominantly as calcite cement which is much more abundant in the sandstones and siltstones of Unit A.

The low relative elemental concentrations in coal is due to the strong dominance of carbon. Some of this carbon has been burned off in rocks of the char lithotype raising relative elemental concentrations. However, relative elemental concentration values in the char are generally lower than those of the other lithotypes.

Chemical Analysis

Several hundred chemical analyses were done during 1981 on core samples from the Hanna UCG site by Anwal Analytical and Consulting Laboratory, Denver, Colorado. Al, Li, Mg, Rb, Si, Na, and K were analyzed using an Atomic Absorption Spectrophotometer. P was analyzed using a Colorimetric method. Gravimetric methods were used to analyze the sulfur forms and Ca, CuO, CuS, Fe(+2), Pb(Tot), PbO, PbS, Sb, Zn(Tot), ZnO, and ZnS were determined by wet chemical analytical methods. These elements were selected for analysis by U.S. Department of Energy contracting officials for comparison with mineralogy and water quality data. A complete core section was done on CH-133 from 19 ft. to the bottom of the Hanna No. 1 coal (346 ft.). This core section constitutes the only data available to establish preburn concentrations for overburden Unit A. Twenty-three samples were averaged to obtain the preburn values. No postburn data was

Table 6. - Semi-quantitative spectrographic analysis of 20 elements by lithotype, Hanna UCG site

Lithotype (#Samples)	(.02) Fe%	(.02) Mg%	(.05) Ca%	(.002) Ti%	(10) Mn	(.5) Ag	(10) B	(20) Ba	(1) Be	(5) Co	(10) Cr	(5) Cu	(20) La	(5) Ni	(10) Pb	(5) Sc	(10) V	(10) Y	(10) Zr	(10) Ga
Sandstone (52)	2.3	1.4	2.55	0.22	617	N	31	858	1.4	9	*43	13	44	*18	21	11	55	30	256	66
Siltstone (51)	3.1	1.7	1.46	0.33	671	*L	73	882	1.5	12	65	24	48	33	27	13	95	34	290	130
Mudstone (9)	3.1	2.8	0.32	0.34	491	*L	76	867	1.5	13	63	36	43	30	34	14	106	31	244	153
Shale (10)	2.6	1.4	0.30	0.41	327	*L	92	860	1.5	13	114	47	67	44	43	16	142	35	222	165
Coal (153)	0.8	0.4	0.28	0.09	96	*L(N)	27	234	*L	*L(N)	*33	17	*L	*8	20	*5	53	*14	47	*L
Char (21)	1.9	0.7	0.85	0.20	205	N	*34	463	1.7	*7	82	33	*49	17	27	12	94	34	99	*37
Paralava (8)	5.3	1.0	1.59	0.55	394	N	81	938	1.5	22	144	136	73	53	37	23	174	53	313	55

Remarks: All values reported in ppm unless otherwise specified
L - detected, but below detection limit (shown in parentheses)
N - not detected
N(L) - majority of data reported as N, but some L values listed
L(N) - data listed about equally as L and N
* - where letter denotations and numerical values are listed, the average was calculated by assigning N a value of zero and L a value of $\frac{1}{2}$ the detection limit

available for Unit A, so the preburn values are included for the purpose of comparison to the preburn and postburn coal values. The preburn averages for the Hanna No. 1 coal were calculated from 124 samples from coreholes CH-131, CH-132, CH-133, CH-134, 2HP-170, and 2HP-171. Values for postburn char were averaged from 22 samples taken from coreholes 2HP-172, 2HP-173, 2HP-174, and 2HP-176. Average elemental concentrations for paralava were calculated from 11 samples taken from coreholes 2HP-172 and 2HP-176. The results are shown in Table 7.

Table 7 shows that the preburn Unit A is highest in the concentrations of Ca, Pb(Tot), PbS, Mg, K, S(ide), and Zn(Tot). Unit A has the lowest average concentrations of CuO, PbO, Li, SO₄, S(H₂O), and Sb. For most elements, Unit A has significantly higher average concentrations than the preburn Hanna No. 1 coal. Exceptions to this general trend are CuO, PbO, Li, SO₄, S(Tot), S(H₂O), and ZnS and Sb. Comparing average elemental concentrations of Unit A to postburn char shows the same general trend as above, only with the magnitude of differences decreasing and more exceptions arising, namely Al, CuS, Fe(+2), P, Na, and ZnO.

Several trends are apparent when average elemental concentrations are compared for the sequence of preburn coal to char to paralava. This sequence may be used to establish the geochemical characteristics and pyrolysis processes of the coal at various stages of increasing temperature. The first trend is a continuous rise in average elemental concentrations from preburn coal through the entire sequence. This is the case for Al, CuO, CuS, Li, Mg, K, Si, Sb, and Na. These elements are commonly present in high temperature stable minerals (i.e. quartz, plagioclase, and feldspar). The increase in average concentrations from preburn coal to char is caused by the burning off of carbon during gasification and the increase seen from char to paralava is due to the rebonding of these elements to form the previously mentioned high temperature stable minerals.

For the elements Fe(+2), Pb(Tot), PbO, PbS, P, SO₄, S(Tot), S(H₂O), S(ide), and ZnO, an increase from preburn coal to char is followed by a decrease from char to paralava. The initial increase in average elemental concentrations from preburn coal to char is again due to the burning off of carbon. The decrease from char to paralava shows that these elements have been released into process effluents by the total breakdown of carbonate and sulfurous minerals (i.e., siderite, gypsum, and pyrite). This breakdown is also supported for iron and sulfur species by preliminary water quality analyses which show large increases in concentrations for these elements in the ground water from baseline to postburn samples (Cooke and Oliver, in press).

Finally, Zn and ZnS show decreases in average elemental concentrations through the sequence while Ca and Rb show an initial decrease from preburn coal to char followed by an increase from char to paralava. For Ca, this represents an initial driving off of secondary calcite from the coal followed by a rebonding in calcic-magnesium aluminosilicate minerals stable at the high temperatures represented by the paralava.

Table 7. - Average concentration values, Hanna UCG site
(Chemical analysis)

Unit (# samples)	Al	Ca	(3) CuO	(3) CuS	(3) Fe(+2)	(3) Pb(Tot)	(3) PbO	(3) PbS	(5) Li	Mg	(50) P	K
Preburn Unit A (23)	7.8%	2.73%	*8	15	1.4%	52	*3	49	10.9	3.09%	*77	2.25%
Preburn coal (124)	2.9%	0.56%	16	14	0.9%	22	15	15	57.6	0.31%	*76	0.35%
Postburn char (22)	7.8%	0.40%	*27	36	2.2%	36	*17	*23	*70.6	0.64%	*208	0.49%
Postburn paralava (11)	14.5%	0.60%	36	42	1.9%	25	*11	*18	199.1	1.12%	203	0.62%

Unit (# samples)	(1) Rb	Si	Na	SO ₄	S(Tot)	S(H ₂ O)	S(ide)	(1) Sb	Zn(Tot)	(3) ZnO	(3) ZnS
Preburn Unit A (23)	51	32.7%	0.52%	0.63%	0.50%	0.29%	0.90%	*1	65	36	33
Preburn coal (124)	*32	4.1%	0.44%	1.95%	0.85%	0.60%	0.56%	*12	63	27	42
Postburn char (22)	*7	17.1%	0.70%	2.57%	1.05%	0.77%	0.79%	*32	59	38	*29
Postburn paralava (11)	*72	32.9%	1.00%	1.26%	0.36%	0.44%	0.19%	66	40	35	*8

Remarks: All values reported in ppm unless otherwise specified

* - values in the data denoted with "<" were valued equal to the number

Only 60 samples were used for preburn coal values on SO₄, S(Tot), SH₂O, S(ide)

SO₄ = sulfate; S(Tot) = total sulfur; SH₂O = water soluble sulfur; S(ide) = sulfide

Detection limits shown in parentheses

A last analysis of Table 7 shows that paralava has the highest average elemental concentrations for Al, CuO, CuS, Li, Rb, Si, Na, and Sb and it has the second highest concentrations of Ca, Fe(+2), Mg, P, and K. This trend (especially for Al, Si, Na, Ca, Fe(+2), and Mg) is indicative of the abundance of high temperature minerals found in paralava samples (i.e., aluminosilicates, calcic-magnesian silicates, magnetite, and various quartz forms).

Proximate and Ultimate Analyses

Standard ASTM proximate and ultimate analyses were done on over 200 coal samples from the Hanna site by Wyoming Analytical Laboratories, Inc., Laramie, Wyoming. Average values for preburn (unaltered) proximate and ultimate analyses of the Hanna No. 1 coal were obtained from 115 samples taken from coreholes CH-133, 2HP-170, 2HP-171, and CH-202. CH-133 is located to the southeast of the Hanna IV experiment (see Figure 1), 2HP-170 was drilled 10 feet northeast of the Hanna II Phases 2 and 3 cavity, 2HP-171 is 15 feet to the southeast of the Hanna II Phases 2 and 3 cavity, and CH-202 is located about 10 feet southwest of Hanna III. Average postburn (heat-altered) values were calculated from samples taken from cores from the Hanna II Phases 2 and 3, and the Hanna III gasification cavities. Fifty-four samples were used for the proximate analysis averages and 55 samples for the ultimate analysis values. The results are shown in Table 8.

The values from Table 8 are shown graphically in Figures 10 and 11. The proximate analysis (Figure 10) shows an increase in ash percentage from unaltered to heat-altered coal and a decrease in volatiles. The percentages of moisture and fixed carbon remain essentially unchanged. Gasification drives off volatiles and a resulting increase in relative ash abundance occurs. Only a minor amount of fixed carbon is oxidized. The ultimate analysis (Figure 11) shows the same increase in ash concentration as in the proximate analysis. Significant decreases in carbon, oxygen, and hydrogen percentages are shown while nitrogen and sulfur remain essentially unchanged. Carbon, oxygen, and hydrogen are driven off during gasification with a resultant rise in ash percentage.

Comparing the fixed carbon percentage from the proximate analysis to the total carbon percentage from the ultimate analysis for the unaltered coals shows that approximately 16% of the total carbon present is free carbon. It would appear by comparing the two graphs shown in Figures 10 and 11 that most of the carbon oxidized during gasification is free carbon as little change in fixed carbon is shown in Figure 10.

A direct relationship also exists between the magnitude of the average changes shown in Figures 10 and 11 and the temperature affecting the coal. A higher temperature would cause greater increases in ash percentage and greater decreases in carbon and volatiles percentages than would a lower temperature. Figures 12 and 13 illustrate this concept graphically as increasing temperature is indicated from right to left. Figure 12, for example, illustrates ash percentages increasing from approximately 25% for corehole 173, to 35% for corehole

174, to 65% for corehole 172, to nearly 70% for corehole 176. Meanwhile, volatiles decrease from about 23% to 9% to 5% to approximately 1% for the same corehole sequence. Carbon percentages also decrease from 52% to 45% to 20% to 19%. The same characteristics are illustrated by Figure 13 for ash and carbon. The anomalous character of the volatiles percentages remains unexplained. The extent of changes in ash, carbon, and volatiles percentages could be used to aid in determining temperatures attained in different areas of a gasification cavity.

Table 8. - Preburn and postburn proximate and ultimate analyses

PROXIMATE (As received)				
Parameter	Unaltered coal	# Samples	Heat-altered coal	# Samples
Moisture	10.76	115	9.83	54
Ash	25.94	115	46.80	54
Volatile matter	31.81	115	13.00	54
Fixed carbon	31.29	115	30.38	54

ULTIMATE (As received)				
Parameter	Unaltered coal	# Samples	Heat-altered coal	# Samples
Hydrogen	5.26	115	3.12	55
Carbon	47.52	115	34.61	55
Nitrogen	1.10	115	1.00	55
Sulfur	0.68	115	0.63	55
Oxygen	17.09	115	9.60	55
Ash	25.94	115	46.82	55
Note: values presented in percent				

PROXIMATE ANALYSIS

Figure 10. Preburn versus postburn proximate analysis values.

Figure 11. Preburn versus postburn ultimate analysis values.

Figure 12. Relationship of changes in proximate and ultimate analyses values for Hanna II Phases 2 and 3.

Figure 13. Relationship of changes in proximate and ultimate analyses values for Hanna III.

CONCLUSIONS

1. Magnetite, cristobalite, tridymite, relict alpha-quartz, and glass are common minerals in the pyrometamorphic rocks of the Hanna UCG site.
2. Though abundant in the preburn coal and overburden rocks, no clay, carbonate, or sulfurous minerals are found in the pyrometamorphic rocks.
3. Early in the gasification process and near the advancing burn front, clay, carbonate, and sulfurous minerals in the coal and in Unit A structurally decay, allowing Al, Mg, Fe, and Ca to bond with abundant silicate ions available from the breakdown of clays and the high temperature metamorphosis of quartz, forming the high temperature stable aluminosilicate and calcic-magnesium silicate minerals common in the pyrometamorphic rocks.
4. Comparisons of preburn and postburn oxide concentrations show an increase in SiO_2 concentration with accompanying decreases in Al_2O_3 , Fe_2O_3 , CaO , SO_3 , MgO , and Na_2O in the postburn rocks. This indicates the breakdown of clay, carbonate, and sulfurous minerals. The released iron and sulfur species are detected in increased concentrations in postburn ground water samples. (Some of the sulfur species probably represent dissolved gases, i.e. SO_2 and H_2S).
5. The elements supplied to the rocks in the gasification cavity from the breakdown of minerals in the coal and in Unit A, plus the concentrating effect of carbon driven off through pyrolysis and oxidation, cause an increase in elemental concentrations for Fe, Ti, Ag, B, Ba, Co, Cr, Cu, La, Ni, Pb, Sc, V, Y, and Zr in paralava rocks over preburn values for Unit A. Increases for all the above elements plus Mg, Ca, Mn, and Ga over preburn values for coal are seen for char as a result of carbon removed from the coal by oxidation.
6. For the preburn lithotypes, shale generally has the highest relative elemental concentrations, followed by mudstone, siltstone, sandstone, and coal, respectively. For the four overburden rock types, this is due to a decreasing dominance of clay minerals accompanied by an increasing dominance of quartz. For coal, the low relative chemical concentrations are due to the strong dominance of carbon over other elements.
7. Among all lithotypes, paralava generally has the highest relative elemental concentrations, due to the formation of high temperature stable minerals at the expense of quartz; and char has elemental concentrations which are generally higher than coal, due to the concentrating effect of removing carbon through oxidation, but concentrations generally remain lower than in the other rock types.

8. Al, CuO, CuS, Li, Mg, K, Si, Sb, and Na show increases in concentration from preburn coal to char due to driving off of carbon, and from char to paralava due to rebonding in high temperature stable minerals (especially for Al, Mg, Si, and Na).
9. Fe(+2), Pb(Tot), PbO, PbS, P, SO₄, S(Tot), S(H₂O), S(ide), and ZnO exhibit an increase in concentration from preburn coal to char again due to driving off of carbon, followed by a decrease in concentrations from char to paralava due to the breakdown of carbonate and sulfurous minerals [especially for Fe(+2), SO₄, S(Tot), S(H₂O), and S(ide)]. These elements are released into process effluents.
10. Ca exhibits a decrease in concentration from preburn coal to char due to the breakdown of secondary calcite in the coal, followed by an increase from char to paralava due to rebonding in calcic-magnesium aluminosilicate minerals.
11. The extent of changes in ash, carbon, and volatiles percentages, as compared to preburn levels, could be used to aid in determining temperatures attained in different areas of a gasification cavity.

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APPENDIX

Concentration Profiles of Ash and Elements in Unaltered Coal
from CH-133 at the Hanna UCG Site

ASH

CH-133

ALUMINUM

CH-133

CH-133

BORON

CH-133

CALCIUM

CH-133

CH-133

CH-133

CH-133

MAGNESIUM

CH-133

MANGANESE

CH-133

CH-133

SILICA

CH-133

SODIUM

CH-133

CH-133

CH-133

CH-133

WATER SOLUABLE SULFUR

CH-133

CH-133

CH-133