MASTER

COAL DESULFURIZATION

BY A

MICROWAVE PROCESS

BY

P.D. ZAVITSANOS, J.A. GOLDEN, K.W. BLEILER, AND I.S. JACOBS*

MARCH 1981

WORK PERFORMED UNDER CONTRACT NO. DE-AC22-80PC30142

GENERAL ELECTRIC COMPANY
RESEARCH AND ENGINEERING
RE-ENTRY SYSTEMS DIVISION
PHILADELPHIA, PA 19101

* GENERAL ELECTRIC CO., CORPORATE R&D, SCHENECTADY, NY

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

COAL DESULFURIZATION

BY A

MICROWAVE PROCESS

TECHNICAL REPORT

NOVEMBER 1980 - FEBRUARY 1981

BY

P.D. ZAVITSANOS, J.A. GOLDEN, K.W. BLEILER, AND I.S. JACOBS

RESEARCH PERFORMED FOR THE
U.S. DEPARTMENT OF ENERGY
UNDER CONTRACT NO. DE-AC22-80PC30142

GENERAL ELECTRIC COMPANY
RESEARCH AND ENGINEERING
RE-ENTRY SYSTEMS DIVISION
PHILADELPHIA, PA 19101

DISCLAIMER

This book was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

ABSTRACT

A laboratory size flow reactor has been developed which has been tested on coal samples up to 100g/batch. A modified version of the applicator will increase sample size to 1,000g; when run continuously can handle 500g-1000g/minute.

Recent measurements on typical 1/4" size (particle size) coal has validated previous results which show up to 50% sulfur removal mainly by converting pyrite to FeS which is shown to have strong magnetic properties and the spectral characteristics of pyrrhotite. Subsequent crushing and physical separation steps such as float sink or magnetic separation further reduces the sulfur level (and more effectively than conventional separation).

Crushing of coal (to 30-100 mesh) and further exposure to the microwave field can further reduce the total sulfur level. An 80% to 90% removal is possible with the proper concentration of NaOH and/or multiple exposures. Results are presented for several important Pennsylvania and Kentucky coals. The results evaluated in terms of #S/10⁶BTU suggest that this method has the potential of meeting environmental requirements.

ACKNOWLEDGMENTS

It is with much appreciation and pleasure that we acknowledge the contributions of Dr. H. Thal in the measurement and interpretation of Dielectric Properties.

The enthusiastic support of Drs. Scott Taylor, Albert Dietz and Jeffrey Solash is gratefully acknowledged.

INTRODUCTION

The objective of this report is to briefly describe the highlights of the work as it has progressed in the recent past and describe in more detail progress made since the start of this contract which from the technical viewpoint is a follow-on to work supported by GE, EPA, and DOE.

In this regard the work will address points which relate to coal beneficiation by the use of microwaves in combination with conventional physical separation techniques (such as float-sink and magnetic separation) as well as in combination with a more efficient chemical extraction of sulfur with the use of sodium hydroxide.

THE USE OF MICROWAVES IN COAL DESULFURIZATION

A. THEORY, MEASUREMENTS OF DIELECTRIC PROPERTIES, AND SELECTIVE HEATING

The potential usefulness of microwaves in chemical desulfurization is supported by the physical nature of microwave energy absorption. Microwave power dissipation by a medium is proportional to the imaginary part of the complex dielectric constant (ϵ'') which is a measure of the dissipated power per unit electric field (squared) according to

$$P/V = \pi f \epsilon_0 E^2 \epsilon''$$

where

P is power absorbed

V is volume

f is the applied frequency (1/sec)

ϵ_0 is the permittivity of free space (3.85×10^{-12} farads/m)

E is the electric field (V/m)

ϵ'' is the imaginary part of the complex dielectric constant

In the case of inhomogeneous mixtures, if ϵ'' differs significantly within the mixture, one would expect different heating rates and pressure rise within the various regions and most probably a change in the overall chemistry of the system, as compared to a method of heating based on conduction from the exterior of the sample. In the case of polar molecules ϵ'' is high and one can expect a situation whereby the energy is channeled into the medium primarily via molecules of high dipole moment even though these molecules may be uniformly dispersed. Under conditions of high power density (or pulsing) one expects maximum deviations from equilibrium and perhaps the most interesting effects relative to being able to shift reaction rates advantageously.

It has been shown previously by dielectric measurements on iron pyrite (FeS_2) samples as well as coal and coal + FeS_2 mixtures that FeS_2 absorbs microwave energy at a rate 2-10 times faster than coal. Figure 1 shows the relative "loss factor"* as a function of frequency for FeS_2 and a coal sample from Kentucky #11.

Similar analysis on a Pittsburgh coal (PSOC-294) is shown in Figure 2 showing loss (absorption) maxima at about 3,000 MHz (3 GHz) and 9,000 MHz (9 GHz).

* Responsible for energy absorption and heating.

Figure 1. Loss factor variation.

Figure 2. PSOC-294 coal, 8-14 mesh, dielectric properties.

B. SELECTIVE VOLATILIZATION OF SULFUR COMPOUNDS

In an apparatus, which will be described in a later chapter, the heating of coal by microwaves is described by Figure 3 which describes temperature rise as a function of time. Depending on power level, sample size, and other parameters the apparent bulk temperature of the sample can be stabilized at a level close to but below the thermal destruction of the coal itself. Visual observation of the sample suggests lack of thermal equilibrium among the various regions of the sample.

The response of coal under such conditions was studied with the help of the time-of-flight mass spectrometer. Measurements of relative ion intensities, which correlate with relative evolution rates of gaseous species, are shown in Figure 4. The most interesting observation here is the fact that in the period when water evolution is the dominant process, sulfur compounds such as SO_2 , CS_2 are also generated at a corresponding low temperature of 200°C - 300°C .

Based on these results, which have been reproduced for Lower Kittanning and Kentucky coals, one expects reduction in the sulfur content of treated coal without significant reduction in the energy content.

Desulfurization measurements were made under varying set of conditions in the absence of chemicals other than air and water. Samples of "as-received" coal containing high pyrite sulfur (PSOC-255 Lower Kittanning Seam, PA) and high organic sulfur (PSOC-272 Kentucky #9 Seam, KY) were irradiated in the 1 KW, 2.45 GHz microwave oven system. The extent of desulfurization was measured under the following experimental conditions:

- a) Inert atmosphere (Argon) + H_2O
- b) Oxygen + H_2O
- c) Air + H_2O
- d) Air
- e) Varying particle size - 1/32 to 5/8"

Ten gram samples were used. The samples were contained in a quartz tube (1" dia. x 6") mounted on foam quartz supports in the box applicator of the 1 KW microwave cavity system. The sample tube was fitted with 1/4" plastic hose lines to provide purging and gas sampling during irradiation. Temperature was monitored using a radiation pyrometer which viewed the center of the sampling tube through a 1/2" dia. x 6" radiation trap mounted on the side of the applicator. Mass spectrometer scans in the 1-200 mass range were taken both during and after irradiation. The same sulfur containing species appeared in both cases. The data are summarized in Figure 5 and Table 1.

Figure 3. Bulk temperature of coal during microwave exposure.

Figure 4. Vapor species from microwave irradiated coal.

Figure 5. Microwave treatment of PSOC-255 coal at 1 kW and 2.45 GHz (particle size effects).

TABLE 1. DATA SUMMARY 1 KW, 2.45 GHz MICROWAVE HEATING/MASS SPECTROMETER SYSTEM

COAL TYPE	GEOGRAPHIC ORIGIN	RUN #	PARTICLE SIZE	EXPERIMENTAL CONDITIONS*				EXPOSURE TIME (SEC.)	HEATING RATE **	MAX TEMP (°C)	% SULFUR LOSS			CALORIFIC VALUE (BTU/LB)	MASS SPECTROMETER DATA (PREDOMINANT SPECIES)							
				H ₂ O	O ₂	AIR	ARGON				TOTAL	NON MAG	MAG		H ₂	CH ₄	H ₂ S	CO ₂	SO	COS	SO ₂	CS ₂
PSOC-255 (PRIMARY PYRITIC SULFUR ~4% TOTAL)	LOWER KITTANNING SEAM, PA.	45*	20-60 M		X			120	S	140	0				X	X	X	X	X	X	X	X
		46*		X			X	140	S	160					X	X	X	X	X	X	X	X
		61				X		180		300	22.1				△	X	X	X	X	X	X	X
		40	1/4"	X	X			110	R	430	----	49.0	+13	NCN MAG 11820 (+ 10.4%)								
* 1 cc H ₂ O ADDED BY SPRAYING + CLOSED SYSTEM 4 PSIG AT END OF RUN # 15 g SAMPLE + 1.5 cc H ₂ O		41		X			X	120	R	230	10.0											
		53		X		X		120	S	310	38.6				△	X	X	X	X	X	X	X
		57		X		X		120	R	340	28.6				△	X	X	X	X	X	X	X
		52		X		X		135	S	160	35.1				△	△	△	X	X	X	X	X
		48		X		X		150	R	460	46.5			11340 (+ 5.9%)	X	X	X	X	X	X	X	X
		50		X		X		200	R	325	39.3											
		51		X		X		260	R	225	41.0				△	△	△	△	△	△	X	△
		58	1/4-3/8"	X		X		90	R	260	31.3				△	X	X	X	X	X	X	X
		60				X		90	R	335	30.8				△	X	X	X	X	X	X	X
		59		X		X		130	R	330	57.3			10580 (- 1.2%)	△	X	X	X	X	X	X	■
		55	1/2-5/8"	X		X		60	R	410	6.1				△	X	X	X	X	X	X	X
		63				X		90	R	530	47.6			11086 (+ 3.6%)	△	X	X	X	X	X	X	X
		56 ^g		X		X		180	S	250	39.4				△	X	X	X	■	X	X	■
PSOC-272	KENTUCKY #9 SEAM-KY.	54	1/4"	X		X		60	R	510	20.6				△	X	X	X	X	X	X	X
		42			X			90	R	375	11.7				X	X	X	X	X	X	X	X
		64				X		180	S	210	33.5				△	X	X	X	X	X	X	X

* ALL COAL SAMPLES 10 g "AS-RECEIVED"
H₂O LISTING MEANS 1cc H₂O ADDED TO
COAL SAMPLE AND PURGE GAS THROUGH
H₂O BUBBLER

** S - SLOW
R - RAPID

X - SPECIES PRESENT

■ - SPECIES NOT PRESENT

△ - NOT COVERED IN MASS SPEC SCAN

A. MOSSBAUER SPECTROSCOPY AND MAGNETIC SEPARATION

The degree of magnetization (σ) exhibited by pyrrhotite, pyrite, and various treated and untreated coals is shown in Table 2. Attention is drawn to the increased value of σ upon microwave irradiation of PSOC-255 coal. Also, pyrite + oil + microwaves yields a degree of magnetization approaching that of highly paramagnetic pyrrhotite. Microwave irradiation of coal has the advantage of raising σ from that associated with FeS_2 to the enhanced degree of magnetization associated with pyrrhotite. This effect offers the possibility of irradiating coal and separating the inorganic sulfur by means of a mild magnetic field.

Mossbauer spectroscopy has been used to investigate changes induced in the coal structure as a result of microwave irradiation. Results associated with the sink portion of as-received PSOC-255 coal and the sink portion of microwave irradiated PSOC-255 coal show that in the former case no trace of paramagnetic pyrrhotite is in evidence while microwave treated coal possesses the magnetic characteristics of pyrrhotite.

In Table 3 are summarized the results from Mossbauer spectrometry along with data on the magnetization per gram in zero field, σ_0 . Included in the table are the relative total absorptions (area "under" the curve) which are proportional to total Fe, and the relative distribution of the phase found (from areal estimates). Table 4 shows a series of measurements on sulfur removal and magnetic properties for magnetic and non-magnetic fractions as obtained by the Franz Isodynamic Separator.

The major significance of these results is based on the fact that significant amounts of pyrite FeS_2 are converted to pyrrhotite (Fe_{1-x}S) which can be easily removed by those of a weak magnetic field. The high magnetic susceptibility of pyrrhotite (existing in contact with pyrites) can greatly benefit magnetic separation in terms of relaxing the requirement for high gradient magnetic fields which are required in order to separate pyrite from coal.

B. MAGNETIC SEPARATION

The previous series of experiments showed a) significant reduction in the sulfur by direct exposure to microwaves, and b) significant conversion of FeS_2 to FeS accompanied with a drastic increase in magnetization. It is apparent that the results suggest an increase in calorific value, a reduction in the sulfur level, enhancement of magnetic properties of the coal sample, which allows further reduction in sulfur and ash by a simplified magnetic separation step. This is a significant result because to our knowledge this is the first time anyone has succeeded in bringing about conversion of pyrite to pyrrhotite using energy in microwave (or RF) range.

TABLE 2. MAGNETIC DATA ON SULFUR-CONTAINING SPECIES*

<u>SAMPLE</u>		<u>σ_{RT} (10 kOe)</u> <u>emu/g</u>	<u>COMMENTS</u>
Fe_7S_8 (PYRRHOTITE)		13	
Z-1	MINERAL FeS_2	-	NOT MEASURABLE
Z-2	MINERAL FeS (FERROUS SULFIDE)	-	NOT MEASURED BUT EXPECTED HIGH
Z-3	MINERAL FeS_2 HEATED TO 600°C (VAC)	2.75	
Z-4	MINERAL FeS_2 HEATED TO 500°C IN O_2	4.13	
Z-5	MINERAL FeS_2 + OIL + M.W.	7.52	1/4 OF Fe IN PYRITE PHASE
Z-6	COAL PSOC-255 + M.W.	1.13	MAG FRACTION
Z-6A	COAL " "	0.15	NON-MAG FRACTION
Z-7	COAL " "	0.73	MAG FRACTION
Z-7A	COAL " "	0.21	N.M. FRACTION
Z-8	COAL " "	0.86	MAG FRACTION
Z-8A	COAL " "	0.05	N.M. FRACTION
Z-9	COAL " "	0.10	NO SEPARATION

* ALL TREATED SAMPLES EXHIBITED MAGNETIC SATURATION.

TABLE 3. PHASES IDENTIFICATION

SAMPLE/RUN#, COND 'N (WT. FRACTION IN %)	TREAT. ATM.	MAG. σ_0 emu/g	PHASES (MOSSBAUER SPEC.)	RELATIVE DISTRIBUTION (%)	RELATIVE TOTAL AREA, F_e (ARB. UNITS)
G /63, UNSEP.	AIR	0.11	$\text{FeS}_2/\text{Fe-OXIDE}$	67/33	0.79
H /62, UNSEP.	AIR	0.53	$\text{FeS}_2/\text{Fe-OXIDE}$	40/60	2.5
A-1/69, UNSEP.	ARGON	0.064	$\text{FeS}_2/\text{Fe}_{1-x}\text{S}$	33/67	1.61
B-1/69, MAG (24%)	ARGON	0.20	$\text{FeS}_2/\text{Fe}_{1-x}\text{S}$	27/73	3.08
C-1/69, NON-MAG (76%)	ARGON	0.018	$\text{FeS}_2/\text{Fe}_{1-x}\text{S}$	62/38	1.14
D-1/70, UNSEP.	ARGON	0.035	FeS_2^*	$\sim 100-\epsilon$	0.62
E-1/70, MAG (2%)	ARGON	0.78	$\text{FeS}_2/\text{Fe}_{1-x}\text{S}$	75/25	4.4 ± 0.2
F-1/70, NON-MAG (98%)	ARGON	0.014	FeS_2	$\sim 100-\epsilon'$	0.26

* ALSO Fe IN CLAY (TYPICAL OF VIRGIN COAL). AMOUNT SYMBOLIZED AS ϵ .

TABLE 4. MAGNETIC SEPARATION RESULTS - PSOC-255

	<u>CALORIFIC VALUE</u> (BTU/# DRY)	<u>% SULFUR & FORMS</u>	<u>MAGNETIC</u> <u>% WEIGHT</u>	<u>NON-MAGNETIC</u> <u>% WEIGHT</u>
AS-RECEIVED (PSOC-255)	10,705	4.2 (2.66 - PYRITIC 1.61 - ORGANIC)	INSIGNIFICANT	~100

<u>RUN NO.</u>	<u>MICROWAVE TREATED, UNSEPARATED</u>		<u>MICROWAVE TREATED, SEPARATED</u>			
	<u>CALORIFIC VALUE</u> (BTU/# DRY)	<u>% SULFUR</u>	<u>MAGNETIC</u> <u>% WEIGHT</u>	<u>NON-MAGNETIC</u>		
				<u>% WEIGHT</u>	<u>% SULFUR</u>	<u>% FORMS</u>
133	12,050	2.36	14.4%	85.6%	1.68	(0.88 - PYRITIC 0.8 - ORGANIC)
136	11,450	2.19	11.3%	88.7%	1.73	(0.95 - PYRITIC 0.78 - ORGANIC)
138	12,630	3.15	10.0%	90.0%	2.60	(1.93 - PYRITIC 0.67 - ORGANIC)

Additional measurements on the degree of magnetization and desulfurization from direct exposure to microwaves are shown in Table 5 for PSOC-255.

C. OTHER CHARACTERIZATION MEASUREMENTS

The question of sulfur removal and calorific value changes in combination with microwave heating followed by crushing and magnetic separation was further pursued as shown in Table 6 for Lower Kittanning and Kentucky #9 coals. The conclusion is that by improving the magnetic separation step one can achieve up to 80% reduction in the total level of sulfur with simultaneous increase in the calorific value of the fuel. It is also obvious that certain sulfur reduction is achieved in the magnetic portion of the sample which suggests that too much clean fuel is dragged by the highly magnetic particles.

These results are very encouraging because by improving the separation step one could develop an even more effective process free of any chemical addition. Because of its simplicity the expected cost would be modest.

In pursuing the physical separation possibilities (after the microwave exposure step), a limited amount of work was done on using separation by density gradients. The effects of microwave exposure followed by float/sink at 1.6g/cc and magnetic separation are shown in Figure 6 where extensive cleaning and energy recovery can be accomplished.

TABLE 5. MAGNETIC PROPERTIES OF PSOC-255 COAL

SAMPLE	RUN NUMBER	BAG	WT. OF SAMPLE	WT. FRACTION	WT. % SULFUR REMOVED	MAG. MEASUREMENT	
						σ_0 * emu/g	σ_1 koe emu/g
A-1	69	TREATED (NOT SEPARATED)	--		52%	0.064	0.070
B-1	69	MAGNETIC (FRACTION)	0.976 gm	24%		0.200	0.221
C-1	69	NON-MAGNETIC (FRACTION)	3.122	76%		0.018	0.020
D-1	70	TREATED (NOT SEPARATED)	--		61%	0.035	0.035
E-1	70	MAGNETIC (FRACTION)	0.119 gm	2%		0.781	0.833
F-1	70	NON MAGNETIC (FRACTION)	5.738	98%		0.014	0.018
G-1	71	TREATED (NOT SEPARATED)	--		43%	~0	~0
H-1	71	MAGNETIC (FRACTION)	0.049 gm	~ 1%		0	0.151
I-1	71	NON MAGNETIC	5.695	~99%		0	~0.005

* σ_0 VALUES CALCULATED BY EXTRAPOLATION BACK TO $H = 0$ FROM σ DATA BETWEEN 10 and 20 kOe

TABLE 6. CALORIFIC VALUE AND SULFUR REMOVAL DATA BY MICROWAVE TREATMENT FOLLOWED BY MAGNETIC SEPARATION

								PSOC-255	
								→ UNSEPARATED 10705 BTU/lb	
								→ NON MAGNETIC 10943 12.2	

TABLE 6. (CONTINUED)

							PSOC-255		
							CALORIFIC VALUE (BTU/lb)		
							AS RECEIVED		
							UNSEPARATED	10705 BTU/lb	
							NON MAGNETIC	10943 42.7	
							TREATED		
COAL TYPE	GEOGRAPHIC ORIGIN	RUN #	PARTICLE SIZE	% SULFUR LOSS			UNSEPARATED	NON MAG	
				TOTAL	NON MAG	MAG	$\Delta CV(\%)$	$\Delta CV(\%)$	
PSOC-255	LOWER KITTANNING SEAM, PA	55	1/2-5/8"	6.1	47.0	12		12415	+16
					46.5	+ 6		13062	+22.0
		70		61.0					
		63		47.6			11086	+3.6	
		* 15g SAMPLE + 1.5 cc H ₂ O		56*	39.4	56.0	**		12240
** NOT ENOUGH SAMPLE FOR S DETERMINATION		68		41.0			11592	+8.3	
				6-61%	31-80%		46.6 AVG.	+13.0 AVG.	

TABLE 6. (CONTINUED)

							PSOC-272		
							CALORIFIC VALUE (BTU/LB)		
							AS RECEIVED		
							UNSEPARATED	13007 BTU/LB	
							NON MAGNETIC	13668 +2.2	
							TREATED		
COAL TYPE	GEOGRAPHIC ORIGIN	RUN #	PARTICLE SIZE	% SULFUR LOSS			UNSEPARATED	NON MAG	
				TOTAL	NON MAG	MAG	ΔCV (Z)	ΔCV (Z)	
PSOC-272	KENTUCKY #9 SEAM, PA	54	1/4"	20.6	20.9	+3.2		13680	+5.2
		42	1/4"	11.7	18.0	13.0			
		64	1/4"	33.5	38.0	31.0			
		65	1/2-5/8"	7.3			13379	+2.8	
							13455	+3.3	
		66	1/2-5/8"				13194	+1.4

Figure 6 . Lower Kittanning Coal microwave treated followed by physical separation.

FLOW REACTOR

A. APPARATUS

In conjunction with this and previous programs a flow reactor was developed which can deliver up to 12 KW, 2.45 GHz of microwave power (into the reaction zone) by a cylindrical microwave applicator as shown in Figures 7 and 8.

The applicator is a stainless steel cylinder 24 inches in length with 1-3/8 inch diameter ports on axis at both ends. The applicator is designed to couple essentially all the power into a single waveguide mode. This empty waveguide mode (TM_{01}) has the maximum electric field on the axis of the cylinder and decreases radially by the bessel function J_0 (2.405 r/a), where r is the radial position and a the radius of the cylinder. Since heating is proportional to the square of the electric field, the empty applicator heating profile will vary as J_0^2 (2.405 r/a).

A quartz purge tube 1-1/4 inch diameter x 150 inches is mounted through the applicator as shown in the diagram. An inert gas (Nitrogen or Argon) is passed through this tube during irradiation of the coal sample. Gases generated from the coal pass from the purge tube and can be further analyzed by mass spectrometry and other conventional means. A modification now in progress involves a gas stream splitting valve mounted at the exit of the tube furnace. This will allow a fraction of the gas to pass through a flame photometer where the emanating total sulfur (in its gaseous forms) will be monitored as a function of time and experimental conditions.

Coal samples to be irradiated are contained in a 1 inch diameter x 30 inch quartz tube. The maximum sample weight is about 100 grams. This size sample covers 24 inches of the sample tube length. The sample tube is placed inside the purge tube and is pulled through the microwave applicator using a motor driven drum and a fiberglass cord. The rate of travel through the field can be varied but at present a single pass through the field corresponds to about 30 seconds of exposure.

B. SYSTEM REDESIGN FOR SCALE-UP EXPERIMENTS

The present Flow Reactor System utilizes a cylindrical microwave applicator 24" in length x 4" diameter, however, the ends of the cylinder are stepped down to 1-3/8" diameter in order to trap the microwave radiation. This arrangement is capable of treating up to 100g of coal samples at 1-2 KW power level. The current contract requires scale-up to accommodate 500-1000g sample size, therefore it is necessary to operate at higher microwave power levels (up to 12 KW) and to increase the diameter of the microwave power traps.

There are two 6 KW, 2450 MHz microwave generators on hand to provide the power needed for the scale-up experiments. In addition, a microwave trap has been designed which will attenuate the 12 KW upper level to .012 milliwatts at the open ends of the cylindrical applicator. This trap has a 3-1/2" diameter

Figure 7. Flow reactor system.

Figure 8. Photograph of flow reactor system.

opening. A diagram of the trap is shown in Figure 9. The unit consists of three donut shaped cavities attached to a 4" diameter copper pipe. Each cavity reduces the microwave power 30 decibels (factor of 1000). The cavity width is 1/8 wave and the spacing is 1/2 wave. The depth is nominally 1/4 wave. This dimension will be 1/4 wave or less and must be determined empirically. Two of these trap assemblies have been constructed and are ready to be checked out in the Flow Reactor System.

The modified flow reactor assembly is shown in Figure 10. The chokes, as previously described, are placed at each end of the microwave applicator. Further design modification will replace the moving batch concept with a continuous feed system capable of treating 0.5-1 kg/minute.

C. EXPERIMENTAL RESULTS

The previously described apparatus has been used to treat coal of various particle sizes as well as under different conditions. The results to date a) confirm data obtained with smaller samples in box type applicators at 0.9, 2.45, and 8.5 GHz; b) show coupling and sulfur reduction for large particles 1/4"-1/2" without the addition of caustic (or any other chemical); c) confirm that when pulverized coal is wetted by NaOH solution and run in microwave apparatus constitutes the most effective means of reducing the sulfur level, pyritic as well as organic, especially when the NaOH concentration is increased or multiple exposure is used (with washing between exposures).

In an effort to summarize important results and point out trends which appear to be most promising, data on several coals will be presented in figures and tables which follow.

Figure 11 shows the behavior of Lower Kittanning Coal (PA Seam PSOC-255). Exposure of large particles (0.25"-0.75") to the field without alkali can remove up to 50% of the sulfur. When the coal is crushed and run in the presence of NaOH sulfur reduction can reach the level 65%-70% depending on exposure times and/or particle size. When the coal is first run in large particles then crushed and run with alkali a single exposure can decrease the sulfur to the 80% level. Table 7 shows this sequence in more detail. It is expected that repetition of the last step can further reduce the sulfur level with an obvious penalty on cost.

Figure 12 shows similar data on Pittsburgh Seam (PSOC-294), Sewanee Seam, Tennessee (PSOC-299), Clintwood Seam, Virginia (PSOC-267) and two Clarion County, Pennsylvania coals #2 and #6. The importance of these results rests on the fact that large mesh (30-60) coal can be handled by this technique. Table 8 presents the sequence which can most effectively be utilized for best results. Further exposure or reduction in particle size can further reduce the sulfur level. This work will be pursued in the near future.

Figure 13 presents results on two Kentucky coals #9 and #11 which again suggest that higher alkali concentration (0.16%), lower particle size and multiple exposures.

MICROWAVE POWER CHOKE SYSTEM FOR 2450 MHz (4.82" WAVELENGTH) RADIATION

Figure 9. Microwave power trap diagram.

25

Figure 10. Modified flow reactor.

Figure 11. Sulfur reduction under different conditions and particle size.

TABLE 7. SULFUR REDUCTION SEQUENCE - PSOC-255

Figure 12. Sulfur reduction.

TABLE 8. SULFUR REDUCTION SEQUENCE - PSOC-267

Figure 13. Sulfur reduction of Kentucky coals

Table 9 shows the sequence of two runs which in combination with washing of coal prior to treatment can reduce the sulfur level in Kentucky #11 by 80%-90%.

Tables 10 and 11 present additional data on calorific values and calculations of lbs of sulfur per million BTU's ($\#S/10^6$ BTU) for the as-received (by G.E.) coal and the cleaned fuel. Combination of Tables 10 and 11 present a strong argument that this method has the potential of meeting environmental standards.

In an effort to compare the effectiveness of caustic in coal cleaning, an effective diffusion rate was calculated from sulfur reduction data as published by various investigators. This comparison is shown in Figure 14. The trends suggest that temperature is indeed an important factor and the microwave heating presents an important advantage in that it provides overall accelerated rates in low (average) temperature range.

TABLE 9. SULFUR REDUCTION SEQUENCE - WESTERN KENTUCKY #11

TABLE 10. FLOW REACTOR RUNS ON WESTERN KENTUCKY #11 COAL SAMPLES

<u>RUN NO.</u>	<u>EXPOSURE TIME (SEC)</u>	<u>PARTICLE SIZE</u>	<u>ALKALI ADDED</u>	<u>% S</u>	<u>% SULFUR REDUCTION</u>	<u>BTU/#</u>
ROM				5.5		
RAW COAL (WASHED)*	0	AS RECEIVED		3.51	36.4	13,244
281	155	AS RECEIVED PLUS ALKALI	X	2.14	61.1	
RAW COAL (WASHED)		1/8"-1/4"				13,266
266	115	1/8"-1/4"		2.84	48.4	
278	120	1/8"-1/4"		3.24	41.1	
RAW COAL (WASHED)	0	30-100 MESH				13,261
267	165	30-100 MESH	X	1.94	64.7	
268	140	30-200 MESH	X	1.74	68.4	11,952
270	200	30-100 MESH	X	2.84	48.4	
273	170	30-100 MESH	X	1.75	68.2	12,165
301**	115	30-100 MESH	X	.85-.42	85-92	12,500
306**	200	30-100 MESH	X	2.53	54.0	} MEASUREMENTS IN PROGRESS
310		30-100 MESH	X	1.97	64.2	
314			X	0.99	83.0	

* WASHED BY TVA

** ALKALI CONCENTRATION - 30%

TABLE 11. SUMMARY OF CALORIFIC VALUE MEASUREMENTS

<u>COAL TYPE</u>	<u>RUN #</u>	<u>RAW COAL</u>	<u>CALORIFIC VALUE (BTU/# DRY)</u>		<u>Δ(CV) (%)</u>	<u>Δ(CV) (%)</u>	<u>#S/10⁶BTU</u>
			<u>MICROWAVE TREATED</u>			<u>Δ(CV) (%)</u>	
<u>PSOC-255</u>	302	<u>11560</u>					<u>3.63</u>
	309					10868	-6.0
	322	<u>13184</u>					<u>2.24</u>
	321		13289		+ .7		2.08
	323		14012		+6.0		1.77
			13158		- .2		1.66
	380A	<u>12372</u>					<u>3.03</u>
	380					14226 (HCl WASH)	+15.0
<u>PSOC-267</u>		<u>13451</u>					<u>4.06</u>
	303					14290	+6.2
<u>PSOC-272</u>	324	<u>13776</u>					<u>2.07</u>
	325		13457		-2.3		1.96
<u>KY #11</u>		<u>13279</u> (WASHED)					<u>2.65</u>
	301					12500	-5.8
	314					12250	-7.7
	314					13543 (HCl WASH)	+2.0

Figure 14. Comparisons of sulfur removal by caustic