DOE/PC/10328-T1

COAL DESULFURIZATION DURING THE COMBUSTION OF COAL/OIL/WATER EMULSIONS: AN ECONOMIC ALTERNATIVE CLEAN LIQUID FUEL

Interim Report, October 1978—November 15, 1979

By
John P. Dooher

November 15, 1979
Date Published

Work Performed Under Contract No. AC22-79PC10328

Adelphi University
Garden City, New York

U. S. DEPARTMENT OF ENERGY

DISCLAIMER

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"COAL DESULFURIZATION DURING THE COMBUSTION OF COAL/OIL/WATER EMULSIONS: AN ECONOMIC ALTERNATIVE CLEAN LIQUID FUEL"

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PREPARED FOR THE UNITED STATES
DEPARTMENT OF ENERGY

Adelphi University
Garden City, New York

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FOREWORD

This report summarizes technical progress accomplished during the second quarter of a one year study being conducted for the Department of Energy under Contract No. DE-Ac22-79PC10328. The work period was October 1, 1978 through April 1, 1979 and was accomplished under the direction of Dr. John P. Dooher, Principal Investigator. Mr. Roy Kurtzrock is the technical representative for DOE.

During this six month period Dr. Dooher worked for 33% of his time on the project, Don Wright 50%, Steve Jakatt 33%, Barbara Gilmartin 75% graduate assistant 50%, and a student assistant 50%.

ABSTRACT

This report represents work accomplished during the first and second quarter of this project to demonstrate "Coal Desulfurization During the Combustion of Coal/Oil/Water Emulsions: An Economic Alternative Clean Liquid Fuel".

The main emphasis during this period was screening candidate emulsions for combustion testing as well as equipment order and set up.

I. OBJECTIVES

A) OVERALL OBJECTIVES

The overall objectives of this program are to develop the use of coal/oil/water mixtures (COW) to the point where sulfur oxides (SO_X) emissions can be controlled in a wide range of applications, such as industrial scale boilers, by simply adding alkaline absorbents to the fuel. Control of SO_X from COW is necessary if we are to implement this very promising fuel alternative to oil.

Secondary objectives of this program are to obtain sufficient data on an actual industrial scale boiler system to prove out the technical feasibility of this process.

The major thrust in this work is the removal of SO_X from stack emissions of this liquid fuel.

B) TECHNICAL OBJECTIVES

The proposed program is planned into Phase I and Phase II. Phase I will extend over a one year period. Phase II which is the second year option is planned to follow Phase I and to be an extension and detailed verification of the Phase I program.

PHASE I 1. Determine optimum economic fuel composition in terms of coal/oil/water and alkaline absorbents for the most efficient removal of sulfur oxides during the combustion of coal/oil/water mixtures in industrial scale boilers.

2. Determine effect of SO_X absorbents on boiler thermal efficiency.

II RESEARCH TO BE PERFORMED BY CONTRACTOR

(a) The scope of work under this contract is unclassified and shall consist of developing the use of coal/oil/water mixtures (COW) to the point where sulfur oxides (SO_X) emissions can be controlled in a wide range of applications. Under Phase I of the program (lasting one year) the Contractor will determine optimum economic fuel composition in terms of coal/oil/water and alkaline abosrbents for the most efficient removal of sulfur oxides during the combustion of coal/oil/water mixtures in industrial scale boilers. Also, the Contractor will determine the effect of SO_X absorbents on boiler thermal efficiency.

The effort under Phase I is composed of the following tasks:

TASK 1. Equipment order and set up: The major areas of equipment needed for data collection and analysis will be ordered and integrated.

TASK 2. Boiler, coal feed, and bag house order and installations: The large boiler, coal feed system and bag house system needed for this work will be ordered and installed.

TASK 3. Rheological Analysis: Various emulsion compositions with added alkali absorbents will be tested for flow properties and stability.

TASK 4. Parametric studies of sulfur oxides removal on laboratory boiler: Small scale laboratory studies will be done to evaluate SO_X removal for various emulsions.

TASK 5. Optimum sulfur oxides removal, fixed emulsion composition, variable alkali absorbent: One concentration of emulsion with four alkali absorbents will be tested for SO_X removal on the large boiler.

TASK 6. Optimum sulfur oxides removal for coal/oil slurry, variable alkali absorbents: Three alkali abssorbents will be tested for SO_X removal in a coal/#4 oil slurry.

TASK 7. Optimization of sulfur oxides removal efficiency with emulsion composition: The composition of coal/oil/water emulsion that will give the optimum sulfur removal efficiency will be determined. This will be done for two alkali absorbents, i.e., soda ash and limestone.

(b) The scope of work shall include such other studies, investigations and services as may be mutually agreed upon.

(c) The Principal Investigator expects to devote the following approximate amount(s) of time to the contract work:

33% or 4 months of a calendar year

III PROGRESS SUMMARY

TASK 1. All major pieces of equipment have been ordered and set up should be completed in July.

TASK 2. A Cleaver Brooks 350HP hot water generator has been ordered and delivery date has been set for June. Arrangements have been made to obtain the bag house.

TASK 3. Several limestone slurries have been screened. A selection of coal/water/#4 oil emulsions has been made for the follow on combustion testing.

TASK 4. The mass spectrometer is being checked out and an immediate start up of combustion tests is anticipated.

TASK 5, 6, 7.

Expected to start in August.

IV PROGRESS DETAILS

TASK 1 - EQUIPMENT ORDER & SET UP:

The major pieces of equipment have been ordered. The GA 1200 Multiple Gas Analyzer has arrived. The sieve shaker was ordered from Fisher Scientific. An electric hoist was ordered from McMaster-Carr. Our purchasing agent is looking for a used fork lift to handle the drums of coal. Used drums have been ordered from Tri-State Street Drum Company in

Graysville, Ga. and are being sent to TVA.

Instrumentation for the boiler will not have long delivery times except the turbine flow meter for the inlet water. We are evaluating the meter produced by Flow Technologies. We have previsously used their smaller models with good results. Pressure transducers will be purchased from American Design Corporation if possible. They have many surplus transducers in stock. The cost is about one-fourth that of new transducers and the delivery time is much shorter. We have been very pleased with the ones we have obtained so far.

Platinum resistance thermometers, thermisters and thermocouples are being evaluated for the various required temperature measurements and will be ordered shortly.

TASK 2. BOILER, COAL FEED AND BAGHOUSE

The Cleaver Brooks 350 hp fire tube boiler has been ordered. Delivery is expected in June. Cleaver Brooks submitted the lowest bid among Kewanee Boiler Corp. and Oswego Package Boiler Company. Eclipse Lookout Company, John Zink Process Systems, ABCO Industries and American Schack Company responded, but sent no bids. Two contractors are submitting bids for installation, one recommended by Con-Ed, the other by Cleaver Brooks. They should be received shortly. Removal of the old boiler will take about four weeks. The installation of the new boiler will take 2 to 3 weeks. Removal will start as soon as the bids are evaluated and a price negotiated.

Three bids have been received for the coal feed system.

We have selected the lowest bid which meets all our requirements.

Although the bag house installation was moved into the second phase, we are working on procuring one and are getting bids for installation.

TASK 3. RHEOLOGICAL

The major thrust of this task is to provide stable, pumpable emulsions for the efficiency tests. Tests are being performed on emulsions of No. 4 oil, coal supplied from TVA, water, and SO_X removal additives. The emulsions are being tested in the Haake Rotovisco RV3 for dyanmic stability and in the ACES pendulum settling device for static stability. Select emulsion will also be placed in a large settling column and their viscosity monitored as a function of time. Using sections of pipe and pressure transducers, the actual pumping characteristics of the emulsions will be ascertained. In this quarter, preliminary work was begun on these investigations.

The coal used in tests was the first sample shipped from the TVA. Because of their sampling procedures, the particle distribution was bi-modal. More than 50% of the coal was larger than 75 microns (200 mesh), while 22% was less than 45 microns (325 mesh). A more typical industrial grind (80% less than 200 mesh) has been promised us and presently being shipped. This smaller coal will be used in all future tests.

Besides the problem with our coal supply, the consistency from batch to batch of the #4 oil obtained from the Adelphi boiler room has been poor. The oil used in the Rotovisco,

pumping and pendulum tests in this report had an apparent viscosity of 106 cP at 356 sec. $^{-1}$. When a new supply of #4 oil was obtained the viscosity dropped to about a third of the original value. In order to duplicate the original oil, #6 and #2 oil were mixed until the proper viscosity was achieved. However the ASTM standard D396-69 for fuel oils gives the kinematic viscosity for #4 oil at 37.8^{o}C as being between 5.8 and 26.4 cSt.[1]. The oil we had been using has a kinematic viscosity of 44.4 cSt which, according to the ASTM, is a light #5 oil. It was decided to fabricate a #4 oil with ν = 16.1 cSt, the middle of the #4 range. This was accomplished by using a standard fuel blending chart. This oil has a dynamic viscosity of 14.29 cp at 234 sec $^{-1}$ and 37.8^{o}C and a density of 0.8891 g/cm^{3}. This oil makes a dynamically stable emulsion with TVA coal as shown in its flow curve, Figure 1. This 40-40-10 COW has an apparent viscosity of 590 cp at 100 sec $^{-1}$.

Using larger TVA coal and higher viscosity #4 oil, Rotovisco tests were performed on emulsion made with different sizes of limestone. A two percent sulfur content was assumed for the emulsion. Concentrations of limestone were used to ideally remove 50%, 100%, and 150% of the sulfur. The particle sizes which were tested were:

a. p < 75 microns
b. p < 53 microns
c. p < 45 microns

Calcium carbonate was ground and sieved in our laboratory for these tests. An industrially ground limestone, Grade "R" York

1. Rose, J.W., Technical Data on Fuel, Scottish Academic Press, 1977, p. 149-150.

White from R.E. Canall, with p < 45 microns, was also tested. The COW used were 40-40-5 and 40-40-10. Of the 19 emulsions tested, only three proved partially satisfactory. These tests will now be repeated using the smaller coal and the lower viscosity #4 oil.

During the testing of the limestone emulsions, a problem arose with the Rotovisco. Highly viscous emulsions would slip down the measuring gap in the viscometer and migrate into the air space under the rotor. This caused a sharp lessening in the measured viscosity of the sample. To rectify this problem, a ribbed rotor and stator has been purchased from Haake. Beside overcoming the slippage difficulty, if there is a wall effect in the Rotovisco due to a layer of oil next to the rotor, it will be eliminated.

Pumping tests were conducted on #4 oil, #6 oil, 35-40-10 and 4-040-10 COW (TVA coal, #4 oil, water) and a 50-50 COM (TVA coal, #4 oil). Five pipes of length 14" and I.D. from 0.163" to 0.356" were used to determine whether a thin layer oil formed next to the pipe resulting in a lower viscosity in the pipe than in the Rotovisco. A 28" pipe with the same I.D. as one of the 14" ones measured the thixotropy of the emulsion under pumping conditions. Flow rate was measure with a graduated cylinder and stopwatch and the pressure monitored with a zero to 300 pound total pressure transducer. The pressure transmitting line between the pipe and transducer was filled with mercury to prevent coal from migrating into the line. As happened in our

large test loop facility, the pressure transmitting line quickly clogged with coal. To overcome this difficulty, we have purchased small tranducers whose pressure sensing surface can be mounted flush in the pipe. These transducers are in the zero to five psi range, which is more appropriate with our short length of pipe. Some data on the 40-40-10 emulsions was collected before the pressure transmitting line was blocked. Both the thixotropic time effect and the "wall" effect seem to be present in this emulsion. When the new transducers are mounted these tests will be repeated.

PENDULUM STUDIES

In order to study the stability of coal/oil/water emulsions and coal/oil mixtures we have developed a physical pendulum a section of which consists of an emulsion sample to determine settling by measuring changes in the period of oscillation. Any settling results in a shift of the center of mass which can be calculated directly from the measure change in the period of the pendulum. This is evident from the equation for the period of the pendulum which is given by:

$$T = 2\pi \sqrt{\frac{I}{MgR}}$$

As the settling results in a shift in R, the position of the center of mass of the pendulum, and a shift in I, the moment of inertia of the pendulum, these shifts in turn result in

changes in T, the period of oscillation. Two independent measurements of the period - permit determination of both unknowns R and I.

Data is obtained through the following procedure. First the period of the empty pendulum and the period of the pendulum with "standard" - a metal rod - are determined. In each instance the pendulum is swung for precisely ten full swings while a counter is totalizing the number of pulses from a 10242.6 HZ frequency source. This step of the procedure is repeated four times for each of the pendulum pivots (upper and lower). From the data an average period is calculated and an uncertainty or spread in values is estimated. By using the empty pendulum and the pendulum with standard object we obtain a measure of the reproducibility of the system from day to day. From these daily variations in the periods of the empty pendulum and the pendulum with standard an uncertainty in the center of mass of the emulsions of $\pm$ 0.02 centimeters exist. This is probably due to a lack of reproducibility in the positioning of the tube within the pendulum.

The data is analyzed by the Burrough's B6700 computer using the program HOYT/NEW PENDULUM III/IV. The program also calculates the mean squared diviation of a group of pulses and the uncertainty of a calculated period.

The PENDULUM/TUBES/A program calculates the periods of the empty glass tubes that will contain the fuel. When analyzed for a series of days, the settling rate of the fuel can be studied by the following the change in the fuel's center of mass. From variations in the periods of the standards, an error of $\pm$ 0.02

centimeters is present in the center of mass of the emulsions. This is probably due to the positioning of the tube in the pendulum.

Appendix 3 gives the shifts in center of mass of the emulsions and slurries. Day 1 is the day of preparation. On average the samples are 16.5 and in length over a period of time. Figure 2 shows the effect of the addition of surfactant to a slurry of 50% TVA coal. The unstabilized slurry settles the most, but the addition of 2% by weight coal of surfactant does not improve the stability. One percent seems to be the optimum concentration. When water is added to the slurry, the long term stability definitely improves with the amount of water up to 15.8% (Figure 3). When the amount of oil is varied in the emulsions (Figure 4) there is a slight long term improvement when an emulsion is made with more coal than oil. Figure 5 shows the effect of the addition of limestone to a 40-40-5 COW. The emulsion with 2.2g limestone with particles less than 45 microns is the most stable while the one with 6.6 of limestone with larger particles settles 4.7 cm in 79 days. All of the limestone emulsions also broke on the Rotovisco.

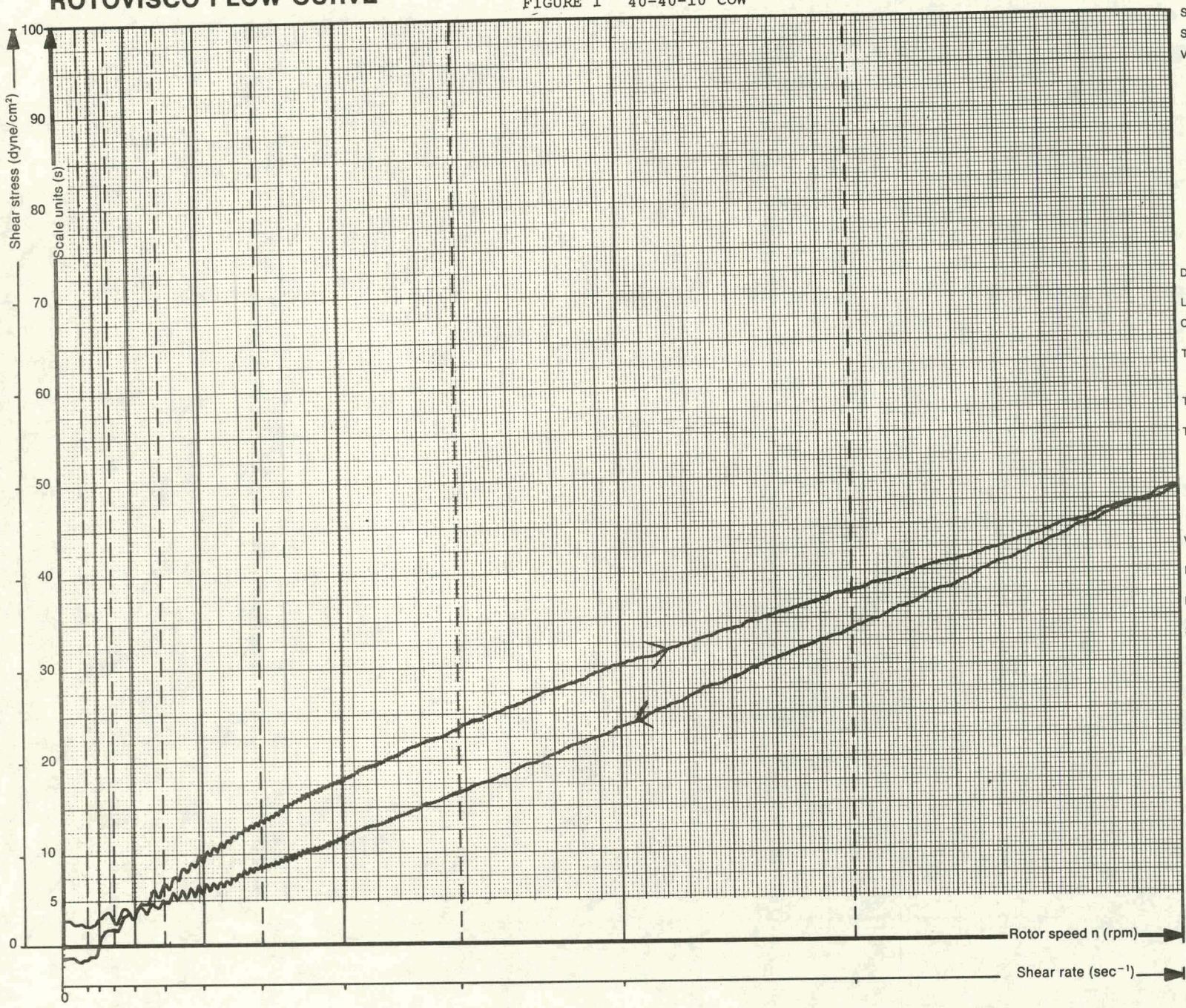
TASK 4 - PARAMETRIC STUDIES OF SO_X REMOVAL ON LABORATORY BOILER

In order to accurately determine the SO_X levels in the combustion gases we have purchased a Mutliple Gas Analyzer. The

instrument has arrived, but it has not been installed. In the meantime we have been re-calibrating the other combustion test monitoring equipment e.g. platinium resistance thermometer, flow meters, and transducers. A procedure is being developed to determine the percentage of ash, moisture, volatiles, sulfur, iron, barium and heat content of the coal. These tests, which will also be performed on the ash deposits in the furnaces are a combination of bomb calorimetry, atomic absorption, and standard chemical techniques.

ROTOVISCO FLOW CURVE

FIGURE I 40-40-10 COW



Shear stress $\tau = A \cdot S$ (dyne/cm²)

Shear rate $D = M \cdot n$ (sec⁻¹)

Viscosity $\eta = \frac{G \cdot S}{n}$ (cp)

HAAKE

Date: 3/29/79

Lab. experiment No.:

Customer:

Test substance: 40-40-10 COW #4

Test temperature: 25°C

Type of circulator: FK

Viscometer assembly:

Rotovisco: RV 3

Measuring head: 50

Sensor system: SV-II

Factor A: 34.6

Factor M: 0.89

Factor G: 3890

RPM program (min⁻²): 200

RPM programmer:

Type of recorder:

Signature:

Remarks: NEW #4 16.1

500 U/S 30 sec. at 75

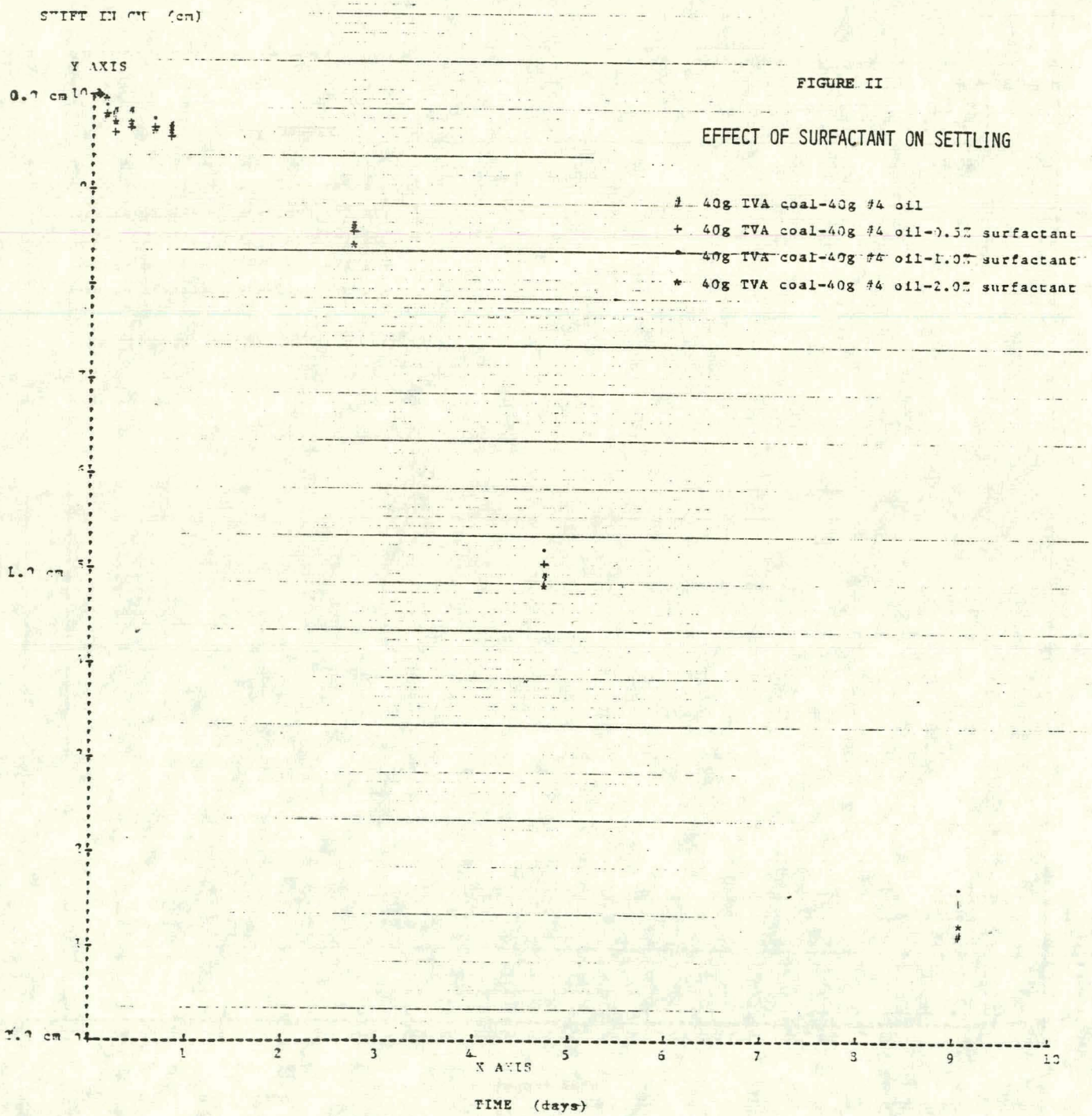


FIGURE II

EFFECT OF SURFACTANT ON SETTLING

‡ 40g TVA coal-40g #4 oil
\+ 40g TVA coal-40g #4 oil-0.5% surfactant
• 40g TVA coal-40g #4 oil-1.0% surfactant
* 40g TVA coal-40g #4 oil-2.0% surfactant

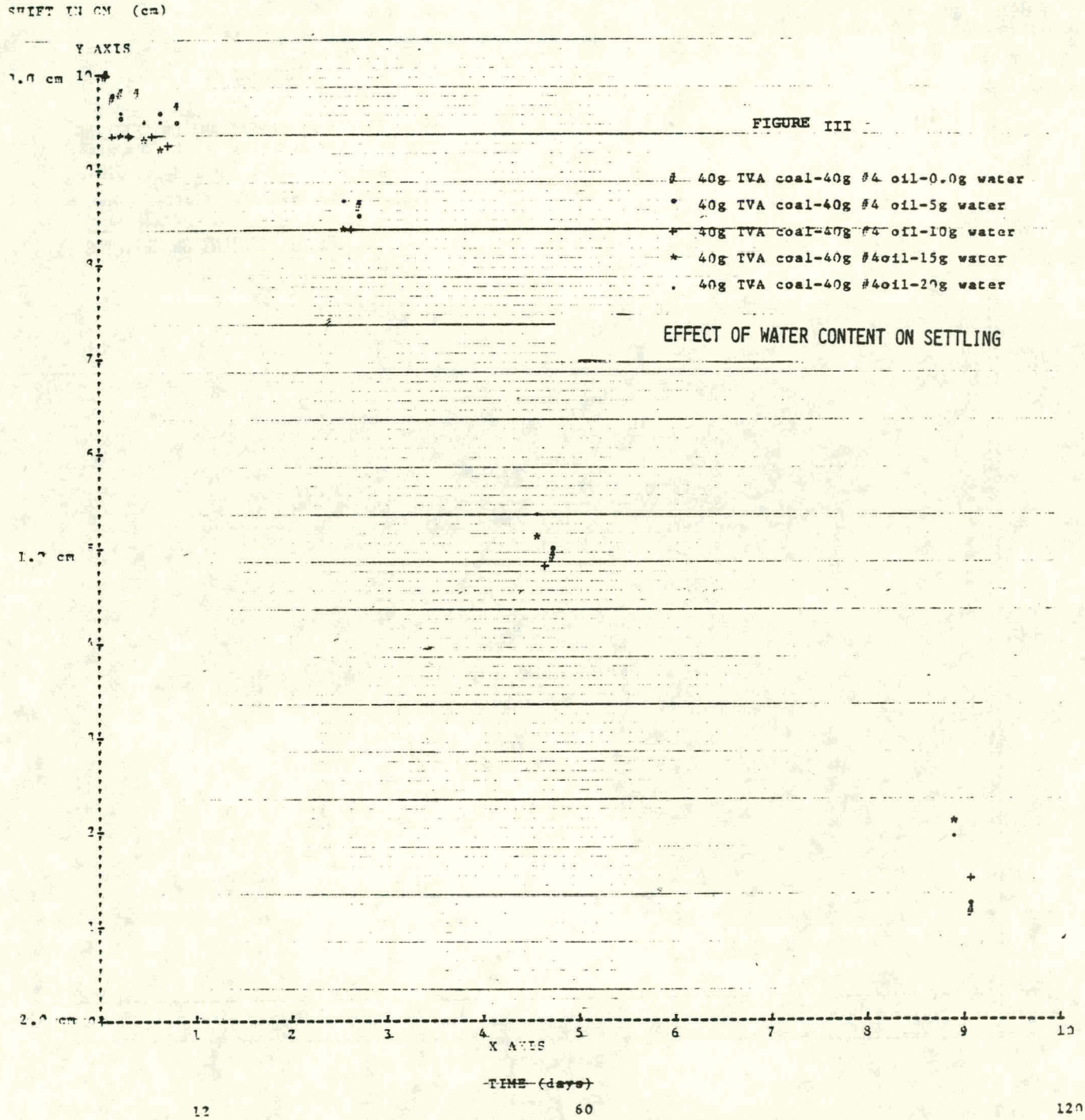


FIGURE III

EFFECT OF WATER CONTENT ON SETTLING

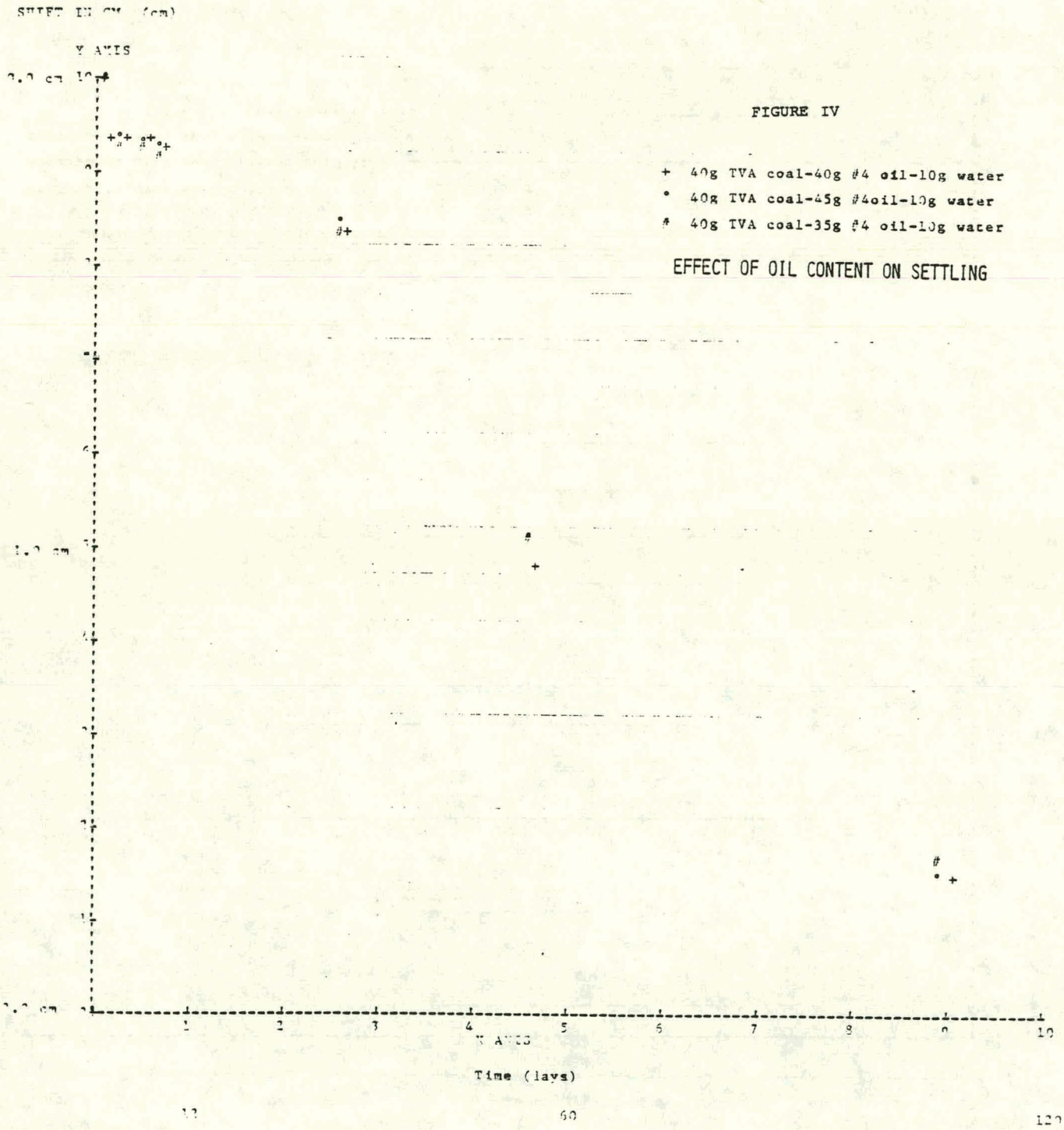


FIGURE IV

\+ 40g TVA coal-40g #4 oil-10g water
• 40g TVA coal-45g #4oil-10g water
\# 40g TVA coal-35g #4 oil-10g water

EFFECT OF OIL CONTENT ON SETTLING

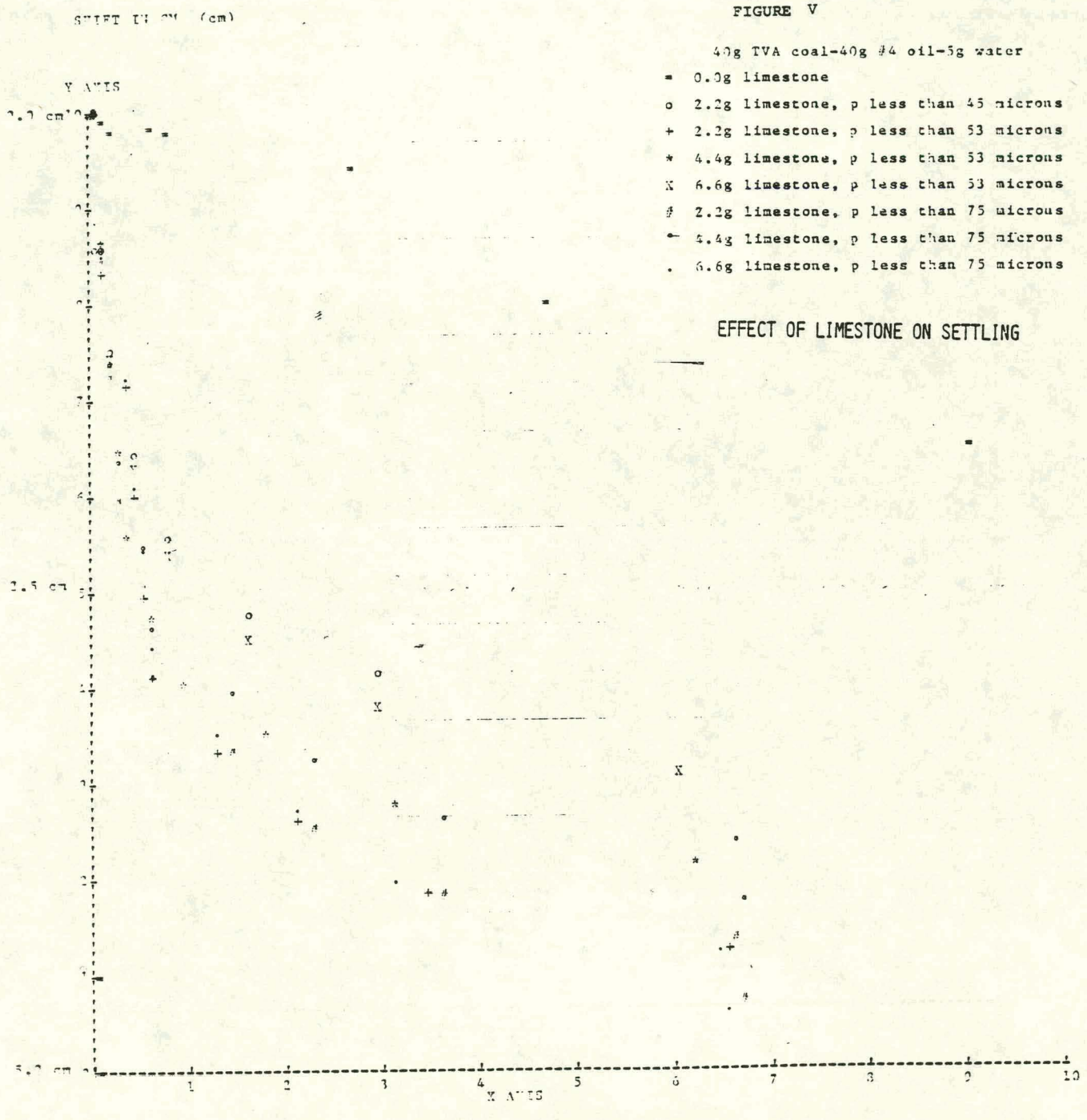


FIGURE V

40g TVA coal-40g #4 oil-5g water

= 0.0g limestone
o 2.2g limestone, p less than 45 microns
+ 2.2g limestone, p less than 53 microns
* 4.4g limestone, p less than 53 microns
X 6.6g limestone, p less than 53 microns
2.2g limestone, p less than 75 microns
— 4.4g limestone, p less than 75 microns
. 6.6g limestone, p less than 75 microns

EFFECT OF LIMESTONE ON SETTLING

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L
100 FILE  99=NEWPNDLUM/DATAALFRED,UNIT=DISK,RECORD=14,BLOCKING=30
200 FILE  6=FILE6,UNIT=REMOTE,RECORD=22
300 SUBROUTINE RATIO(M,M2,ME,T,T1,T2,T21,RE,IE,ALPHA,BETA)
400  REAL M,M2,ME,IE
500 DOUBLE PRECISION T,T1,T2,T21,WR,XR,YR,ZR
600 WR=M*(T1*T1+BETA)*1.339+ALPHA
700 XR=T1*T1-T*T+2.0*BETA
800 YR=M2*(T21*T21+BETA)*1.339+ALPHA
900 ZR=T21*T21-T2*T2+2.0*BETA
1000 RE=WR/ME/XR-YR/ME/ZR
1100 IE=1./4.028*(WR*T*T/XR-YR*T2*T2/ZR)
1200 RETURN
1300 END
1400 SUBROUTINE RATIO1(M1,ALPHA,BETA,T,T1,RI)
1500 DOUBLE PRECISION T,T1,ZR,XR
1600 ZR=T1*T1+BETA+ALPHA/M1/1.339
1700 XR=T1*T1-T*T+2.0*BETA
1800 RI=ZR/XR*1.339
1900 RETURN
2000 END
2100  SUBROUTINE GRAPH(M)
2200  COMMON ITIM(100),Y(100)
2300  DIMENSION K(100),NA(100)
2350  SHIFT(L)=Y(L)-Y(1)
2400  I=1H*
2500  J=1H
2600  N=1H.
2700  DO 1 L=1,100
2800  NA(L)=N
2900  1 K(L)=J
3000  PRINT 7,NA
3100  7 FORMAT(X,"DAYS",103X,"SHIFT IN",/,103X,"CENTER OF MASS",
3200 -X,'IN CENTIMETERS",/,6X,100A1,/)
3300  BIG =Y(1)
3400  SMALL=BIG
3500  DO 2 L=2,M
3600  IF (Y(L).GT.BIG) BIG=Y(L)
3700  IF (Y(L).LT.SMALL) SMALL=Y(L)
3800  2 CONTINUE
3900  RANGE=.5/99.
4000  IF (ITIM(M).LE.20) IA=3
4100  IF (ITIM(M).GT.20.AND.ITIM(M).LE.50) IA=2
4200  IF (ITIM(M).GT.50) IA=1
4300  DO 3 L=1,M
4400  N=(.5+SMALL-Y(L))/RANGE
4500  N=N+1
4600  K(N)=I
4800  PRINT 4,ITIM(L),(K(LA),LA=1,100),SHIFT(L)
4900  4 FORMAT(I4,3X,100A1,3X,F7.4)
5000  IF(L.EQ.M) GO TO 3
5100  ISPACE=(ITIM(L+1)-ITIM(L))*IA-1
5200  DO 5 LB=1,ISPACE
5300  PRINT 6,NA(1)
5400  6 FORMAT(1H ,6X,A1)
```

```
5500  5 CONTINUE
5600  3 K(N)=J
5700  RETURN
5800  END
5900 %PROGRAM HOYT/NEWPNDLUMIII/IV
6000 %CALCULATES THE CENTER OF MASS AND THE MOMENT
6100 %OF INERTIA OF AN EMULSION SAMPLE WITH DATA
6200 %OBTAINED FROM THE ACES PENDLUM.
6300  COMMON ITIM(100),CM(100)
6400  DIMENSION V(2)
6500 DOUBLE PRECISION TALO(7),TAHI(7),PL(12),PM(12),PLS(12),PMS(12),
6600 -AVEPL(15),AVEPM(15),DEL(12),DELM(12),
6700 -DATE,TL,TM,SL,SM,DEVTL,DEVTM,TLMAX,TMMAX,TAT,TATH,
6800 -SMP1,SMP2,SMP3,SMP4,SMP5
6900 REAL MAS(7),M,MTOTAL,MA,MSTAND,IE,MSDLO(12),MSDMID(12),
7000 -IES,IESAVE,M2,M1,ME
7100 DATA(V(K),K=1,2)/4HSPT.,4HPND./
7200 READ(99,/) MAS(1)
7300 READ(99,/) TALO(1)
7400 T1=TALO(1)/1.0019
7500 READ(99,/) TAHI(1)
7600 T2=TAHI(1)/0.99773
7700  READ(99,21) SMP1,SMP2,SMP3,SMP4,SMP5
7800  21 FORMAT (A12,A12,A12,A12,A12)
7900 NPEND1=1
8000 COUNT=0.0
8100 DATA MSTAND/144.2/,F/102426./
8200 WRITE(6,600)
8300  600 FORMAT(X,"ALL MEASUREMENTS IN CGS UNITS",/)
8400  NCOUNT=0
8500  3 READ(99,70,END=12) NTEST,NWDATE,DATE,NPEND
8600  70 FORMAT (I3,X,I1,X,A8,X,I1)
8700 READ(99,4) NTYPE,NTUBE,NRUN
8800  IF(NTYPE.NE.3) GO TO 13
8900  NCOUNT=NCOUNT+1
9000  ITIM(NCOUNT)=NTEST-1
9100 %IS THIS A NEW DATE? YES:NWDATE=1,WRITE HEADING
9200 13 IF(NWDATE.EQ.1) WRITE(6,950) NTEST,DATE
9300  950FORMAT(X,"TEST ",I3,20X,"DATE ",A12,//,X,"TUBE",5X,
9400 -"DEVIATIONS",15X,"AVERAGE PERIOD",16X,"R CM TUBE",6X,
9500 -"R CM SLURRY",5X,"MOMENT TUBE",6X,"MOMENT SLURRY",/,
9600 -10X,"LOWER",2X,"UPPER",10X,"LOWER",14X,"UPPER",/)
9700  4FORMAT(I1,2I2)
9800 READ(99,/)MTOTAL
9900 IF (NPEND.EQ.0) NPEND1=NPEND
10000 IF (NPEND.EQ.1) NPEND2=NPEND
10100 IF (NPEND1.EQ.0.AND.NPEND2.EQ.1.AND.NPEND.EQ.1) TALO(1)=T1
10200 IF (NPEND1.EQ.0.AND.NPEND2.EQ.1.AND.NPEND.EQ.1) TAHI(1)=T2
10300 IF (NPEND.EQ.0) PNDM=295.6
10400 IF (NPEND.EQ.1) PNDM=297.2
10500 M=MTOTAL+PNDM
10600 M2=PNDM+MAS(1)
10700 ME=MTOTAL-MAS(1)
10800 SUMRE=0.
```

```
10900 SUMIE=0.
11000 10 DO 500 J=1,NRUN
11100 READ(99,102) NPOINT
11200  102FORMAT(I2)
11300 SM=0
11400 SL=0
11500 SUMDEL=0.
11600 SUMDEM=0.
11700 DO 100 I=1,NPOINT
11800 %READ IN RAW DATA (PULSES)
11900 READ(99,/) PL(I),PM(1)
12000 %SAVE THESE DATA POINTS WITH PLS & PMS
12100 PLS(I)=PL(I)
12200 PMS(I)=PM(I)
12300 %
12400 PL(I)=SL + PL(I)
12500 SL=PL(I)
12600 %
12700 PM(I)=SM + PM(I)
12800 SM=PM(I)
12900  100 CONTINUE
13000 %AVERAGE THE PULSE VALUES
13100 AVEPL(J)=SL/NPOINT
13200 AVEPM(J)=SM/NPOINT
13300 %COMPUTE PERIODS FROM DATA
13400 TL=AVEPL(J)/F
13500 TM=AVEPM(J)/F
13600 %COMPUTE MEAN SQUARE DEVIATION OF PULSES
13700 DO 400 I=1,NPOINT
13800 DEL(I)=(AVEPL(J)-PLS(I))**2
13900 SUMDEL=SUMDEL+DEL(I)
14000 %REPEAT FOR MIDDLE POSITION
14100 DELM(I)=(AVEPM(J)-PMS(I))**2
14200 SUMDEM=SUMDEM+DELM(I)
14300  400 CONTINUE
14400 MSDLO(J)=SQRT(SUMDEL)/NPOINT
14500 DEVTL=MSDLO(J)/F
14600 MSDMID(J)=SQRT(SUMDEM)/NPOINT
14700 DEVTM=MSDMID(J)/F
14800 %BEGIN CALCULATING SECONDARY PARAMETERS
14900 TLMAX=DEVTL+TL
15000 TMMAX=DEVTM+TM
15100 %USE SECONDARY PARAMETERS TO CALCULATE RE AND IE
15200 %FOR THE TWO RUNS
15300 TAT=TALO(1)
15400 TATH=TAHI(1)
15500 IF(NTYPE.EQ.3) GO TO 7
15600 IF (NPEND.EQ.0) ALPHA=-1.917
15700 IF (NPEND.EQ.1) ALPHA=-2.191
15800 BETA=5.393E-02
15900 IF (NTYPE.EQ.1) M1=MTOTAL+PNDM
16000 IF (NTYPE.EQ.1) MSP=M1
16100 IF (NTYPE.EQ.2) M1=PNDM
16200 IF (NTYPE.EQ.2)MP=M1
```

```
16300 CALL RATIO1(M1,ALPHA,BETA,TL,TM,RA)
16400 IF (NTYPE.EQ.1) RSP=RA
16500 IF (NTYPE.EQ.2)RP=RA
16600 COUNT=COUNT+1
16700 CMPARE=COUNT/2.-FLOAT(IFIX(COUNT/2.))
16800 IF (CMPARE.EQ.0.0) RS=(MSP*RSP-MP*RP)/MSTAND
16900 IE=0.0
17000  GO TO 750
17100  7 IF(NPEND.EQ.0) ALPHA=-1.917
17200  IF (NPEND.EQ.1) ALPHA=-2.191
17300 BETA=5.393E-02
17400 DO 11 K=1,2
17500 CALL RATIO(M,M2,ME,TL,TM,TAT,TATH,RE,IE,ALPHA,BETA)
17600  CM(NCOUNT)=RE
17700 IF (K.EQ.1)IES=IE
17800 IF (K.EQ.1) RES=RE
17900  IF( K.EQ.1) TLSAVE=TL
18000  IF( K.EQ.1) TMSAVE=TM
18100 TL=TLMAX
18200  11 TM=TMMAX
18300 CALL RATIO1(M2,ALPHA,BETA,TAT,TATH,RA)
18400 IESAVE=0.0
18500  DRE=ABS(RES-RE)
18600  DIE=ABS(IES-IE)
18700 WRITE(6,300) NTUBE,MSDLO(J),MSDMID(J),TLSAVE,DEVTL,TMSAVE,
18800 -DEVTM,RA,RES,DRE,IESAVE,IES,DIE
18900  300FORMAT(X,I2,5X,2(F7.0,X),0PF10.7,"+/-",1PE7.1,0PF10.7,
19000 -"+/-",1PE7.1,2X,0PF7.4,7X,0PF7.4,"+/-",1PE7.1,
19100 -X,0PF9.1,2X,0PF9.1,"+/-",1PE7.1)
19200  GO TO 110
19300  750 WRITE(6,800) V(NTYPE),MSDLO(J),MSDMID(J),TL,TM,RA,IE
19400  800FORMAT(A7,X,2(F7.0,X),0PF10.7,10X,F10.7,
19500 -12X,F7.4,25X,F9.1)
19600 IF (CMPARE.NE.0.0) GO TO 110
19700 WRITE (6,801) RS
19800  801 FORMAT(X,"STD.",61X,F7.4)
19900 110 SUMRE=SUMRE+RES
20000 SUMIE=SUMIE+IES
20100 500 CONTINUE
20200  IF(NTYPE.NE.3) GO TO 3
20300 AVERE=SUMRE/NRUN
20400 AVEIE=SUMIE/NRUN
20500 WRITE(6,550) NRUN,AVERE,NRUN,AVEIE
20600 550FORMAT(X,"AVERAGE CM FOR ",I2," RUNS: ",4X,F10.4,/,X,
20700 -"AVERAGE MOMENT FOR ",I2," RUNS: ",F10.1,/)
20800  GO TO 3
20900  12 READ/,ITEST
21000  PRINT 15, ITEST,SMP1,SMP2,SMP3,SMP4,SMP5
21100  15 FORMAT(1H1,////,3X,"TUBE",X,I3,3X,A12,A12,A12,A12,A12,////)
21200  CALL GRAPH (NCOUNT)
21300  STOP
21400 END
#
```

```
L
100 FILE  90=DATATUBES,UNIT=DISK,RECORD=14,BLOCKING=30
105 %PROGRAM PNDLUM/TUBES CALCULATES THE AVERAGE
110 %PERIODS AND PARAMETERS RELATED TO THE
115 %CENTER OF MASS AND THE MOMENT OF INERTIA
120 %FOR THE TUBES ONLY, USED ON THE ACES PENDULUM.
125 DOUBLE PRECISION F
130 DOUBLE PRECISION PL(6,2),PM(6,2),PLS(6,2),PMS(6,2),AVEPL(2),
135 -AVEPM(2),TL(2),TM(2),DEL(6,2),DELM(6,2),MSDLO(2),MSDMID(2)
140  F=102426.
145 %START READING IN DATA
150 5  READ(90,10) TUBE,TRIAL
155 10 FORMAT(A2,X,A2)
160  DO 15 J=1,1
165 SM=0
170 SL=0
175 %
180 DO 20 I=1,5
185 %READ IN RAW DATA (PULSES)
190 READ(90,/) PL(I,J),PM(I,J)
195 %SAVE THESE DATA POINTS WITH PLS & PMS
200 PLS(I,J)=PL(I,J)
205 PMS(I,J)=PM(I,J)
210 %
215 PL(I,J)=SL + PL(I,J)
220 SL=PL(I,J)
225 %
230 PM(I,J)=SM + PM(I,J)
235 SM=PM(I,J)
240 20  CONTINUE
245 %AVERAGE THE PULSES
250 AVEPL(J)=SL/5.
255 AVEPM(J)=SM/5.
260 %COMPUTE PERIODS FROM DATA
265 TL(J)=AVEPL(J)/F
270 TM(J)=AVEPM(J)/F
275 15  CONTINUE
280 %COMPUTE MEAN SQUARE DEVIATION OF PULSES
285  DO 30 J=1,1
290 SUMDEL=0.
295 SUMDEM=0.
300 DO 35 I=1,5
305 DEL(I,J)=(AVEPL(J)-PLS(I,J))**2
310 SUMDEL=SUMDEL+DEL(I,J)
315 %REPEAT FOR MIDDLE POSITION
320 DELM(I,J)=(AVEPM(J)-PMS(I,J))**2
325 SUMDEM=SUMDEM+DELM(I,J)
330 35 CONTINUE
335  MSDLO(J)=SQRT(SUMDEL/5.)
340  MSDMID(J)=SQRT(SUMDEM/5.)
345 30  CONTINUE
350 %COMPUTE THE AVE OF PERIODS FOR TWO RUNS
355  TLAVE=TL(1)
360  TMAVE=TM(1)
```

```
365 %COMPUTE DEVIATIONS OF PERIODS
370  DEVTL=MSDLO(1)/F
375  DEVTHI=MSDMID(1)/F
380 %WRITE MESSAGES AND COMPUTED PERIODS
385 WRITE(6,100)
390 100 FORMAT(X,///,X'ALL MEASUREMENTS IN CGS UNITS',/)
395 WRITE(6,110) TUBE,TRIAL
400 110 FORMAT(X,'TUBE ',A2,5X,'TRIAL ',A2)
405  WRITE(6,120) MSDLO(1),MSDMID(1)
410  120 FORMAT(X,35X,'RUN 1',//,X,'M.S.D. LO POSITION'
415  -'--PULSES',5X,F10.2,/,X,'M.S.D. MD POSITION'
420 -'--PULSES',5X,F10.2)
425  WRITE(6,140) TL(1),TM(1)
430  140 FORMAT(X,/,X,'PERIOD--LOWER POSITION',9X,F10.7,
435  -/,X,'PERIOD--HIGHER POSITION',8X,F10.7)
440  %
445  WRITE(6,130) TLAVE,DEVTL,TMAVE,DEVTHI
450  130 FORMAT(X,/,X,'AVERAGE PERIOD FOR 1 RUN--LOWER POSITION'
455  -,2X,F10.7,X,'+/-',1PE9.1,/,X,
460  -'AVERAGE PERIOD FOR 1 RUN--HIGHER POSITION',X,
465  -0PF10.7,X,'+/-',1PE9.1)
475 %CHECK TO SEE IF THERE IS MORE DATA
480 READ(90,/) IDATA
485 IF (IDATA.EQ.1) GO TO 5
490 STOP
495 END
$
```

APPENDIX 3a

SAMPLE DAY	(0) 40-40-5 & Limestone	(1) 40-40	(2) 40-40-.4S	(3) 40-40 .8S	(4) 40-40-1.6S	(5) 40-40-5	(6) 40-40-10	(7) 40-40-15	(8) 40-40-20	(9) 40-35-10	(10) 40-45-10
1	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2	0.7082	0.0515	0.0368	0.0197	0.0138	0.0452					
3	1.2359	0.0425	0.0770	0.0586	0.0571	0.1015		0.1313	0.0785	0.1453	0.1322
4							0.1289				
5		0.0428	0.0682	0.0655	0.0576						
6	1.7767							0.1431	0.1014	0.1505	0.1386
7							0.1283				
8			0.0693	0.0544	0.0844	0.0866		0.1579	0.0967	0.1715	0.1539
9							0.1507				
10	2.2107	0.0653	0.0854	0.0697	0.0808	0.1148					
20	2.6193										
31								0.3276	0.2653	0.3347	0.3129
32							0.3286				
33	0.2790	0.2861	0.28121	0.3241		0.3077					
36	2.9226										
55								0.9786	0.9276	0.9835	0.9828
56							1.0404				
57		1.0246	0.9939	0.9584	1.0449	1.0134					
107								1.5814	1.6083	1.6642	1.6973
108											
109		1.7712	1.6971	1.6653	1.7513	1.7569	1.7024				

DAY 1 = day of preparation
SAMPLES 15.5 - 17.5 cm long
SHIFTS ± 0.02 cm

APPENDIX 3b

SAMPLE DAY	40-40-5 Limestone 2.2g p<45μ	40-40-5 Limestone 2.2g p<53μ	40-40-5 Limestone 4.42g p<53μ	40-40-5 Limestone 6.6g p<53μ	40-40-5 Limestone 2.2g p<75μ	40-40-5 Limestone 4.4g p<75μ	40-40-5 Limestone 6.6g p<75μ
1	0.00	0.0000	0.0000	0.0000	0.0000	0.0000	0.000
2	0.7082	0.8422	0.6870	0.6992	0.7935	0.7472	0.7507
3	1.2359		1.3103	1.2849	1.3923	1.3312	
4			1.7715		2.0353	1.8406	
5		1.4263	2.2178				1.3931
6	1.7767	2.0025	1.8571				1.9575
7		2.5250			2.4880	2.2891	2.2863
8		2.9421	2.6448		2.9583	2.7122	2.7947
9							
10	2.2107			2.3081			
12			2.9858				
16		3.3386					3.2442
18					3.3413	3.0472	
20	2.6193			2.7529			
22			3.2474				
26		3.3386					3.6429
28					3.7405	3.4044	
36	2.9226			3.1018			
38			3.6179				4.0157
42		4.0748					
44					4.0811	3.7084	
73				3.4541			
75			3.9274				
78							4.3852
79		4.3799					4.6949
80					4.3217	3.8326	
81	Shift are in cm.				4.6439	4.1432	

"COAL DESULFURIZATION DURING THE COMBUSTION OF COAL/OIL/WATER EMULSIONS: AN ECONOMIC ALTERNATIVE CLEAN LIQUID FUEL"

Interim Report for the
Period April 1979 - August 1979

Dr. John P. Dooher

Adelphi University
Garden City, New York 11530

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PREPARED FOR THE UNITED STATES
DEPARTMENT OF ENERGY
Under Contract No. DE-AC22-79PC10328

FOREWORD

This report summarizes technical progress accomplished during the third quarter of a one year study being conducted for the Department of Energy under Contract No. DE-AC22-79PC10328. This contract has been extended to January 31, 1980. The work period was April 2, 1979 through August 31, 1979 and was accomplished under the direction of Dr. John P. Dooher, Principal Investigator. Mr. Roy Kurtzrock is the technical representative for DOE.

During this five month period Dr. Dooher worked for 33% of his time on the project, Donald Wright 50%, Steve Jakatt 33%, Barbara Gilmartin 75%, a graduate assistant 50%, and a student assistant 50%.

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ABSTRACT

This report represents work accomplished during the third quarter of this project to demonstrate: "Coal Desulfurization During the Combustion of Coal/Oil/Water Emulsions: An Economic Alternative Clean Liquid Fuel".

The main emphasis during this period was on the parametric studies of sulfur oxides removal on the laboratory boiler. Instrumentation on laboratory boiler was completed and initial tests were conducted. In addition to our parametric studies of sulfur oxides removal, we found by using the power law, precise apparent viscosities can be obtained from the Roto-visco and pumping tubes and then correlated.

I. OBJECTIVES

A) OVERALL OBJECTIVES

The overall objectives of this program are to develop the use of coal/oil/water mixtures (COW) to the point where sulfur oxides (SO_x) emissions can be controlled in a wide range of applications, such as industrial scale boilers, by simply adding alkaline absorbents to the fuel. Control of SO_x from COW is necessary if we are to implement this very promising fuel alternative to oil.

Secondary objectives of this program are to obtain sufficient data on an actual industrial scale boiler system to prove out the technical feasibility of this process.

The major thrust in this work is the removal of SO_x from stack emissions of this liquid fuel.

B) TECHNICAL OBJECTIVES

The proposed program is planned into Phase I and Phase II. Phase I will extend over a one year period. Phase II which is the second year option is planned to follow Phase I and to be an extension and detailed verification of the Phase I program.

PHASE I 1. Determine optimum economic fuel composition in terms of coal/oil/water and alkaline absorbents for the most efficient removal of sulfur oxides during the combustion of coal/oil/water mixtures in industrial scale boilers.

2. Determine effect of SO_X absorbents on boiler thermal efficiency.

II RESEARCH TO BE PERFORMED BY CONTRACTOR

(a) The scope of work under this contract is unclassified and shall consist of developing the use of coal/oil/water mixtures (COW) to the point where sulfur oxides (SO_X) emissions can be controlled in a wide range of applications. Under Phase I of the program (lasting one year) the Contractor will determine optimum economic fuel composition in terms of coal/oil/water and alkaline abosrbents for the most efficient removal of sulfur oxides during the combustion of coal/oil/water mixtures in industrial scale boilers. Also, the Contractor will determine the effect of SO_X absorbents on boiler thermal efficiency.

The effort under Phase I is composed of the following tasks:

TASK 1. Equipment order and set up: The major areas of equipment needed for data collection and analysis will be ordered and integrated.

TASK 2. Boiler, coal feed, and bag house order and installations: The large boiler, coal feed system and bag house system needed for this work will be ordered and installed.

TASK 3. Rheological Analysis: Various emulsion compositions with added alkali absorbents will be tested for flow properties and stability.

TASK 4. Parametric studies of sulfur oxides removal on laboratory boiler: Small scale laboratory studies will be done to evaluate SO_X removal for various emulsions.

TASK 5. Optimum sulfur oxides removal, fixed emulsion composition, variable alkali absorbent: One concentration of emulsion with four alkali absorbents will be tested for SO_X removal on the large boiler.

TASK 6. Optimum sulfur oxides removal for coal/oil slurry, variable alkali absorbents: Three alkali absorbents will be tested for SO_X removal in a coal/#4 oil slurry.

TASK 7. Optimization of sulfur oxides removal efficiency with emulsion composition: The composition of coal/oil/water emulsion that will give the optimum sulfur removal efficiency will be determined. This will be done for two alkali absorbents, i.e., soda ash and limestone.

(b) The scope of work shall include such other studies, investigations and services as may be mutually agreed upon.

(c) The Principal Investigator expects to devote the following approximate amount(s) of time to the contract work:

33% or 4 months of a calendar year

III PROGRESS SUMMARY

TASK 1. The boiler arrived on August 24, 1979. All major pieces of equipment have been ordered and set up in the laboratory. As soon as the boiler is installed it will be instrumented.

TASK 2. Old Boiler has been removed. Excavation of the boiler room is being planned. The design of the storage tank has been completed.

TASK 3. Using the power law, precise apparent viscosities can be obtained from the Rotovisco and pumping tubes and then correlated.

TASK 4. Instrumentation on laboratory boiler has been completed. A procedure for ash analysis has been developed. Initial tests on laboratory boiler have been performed. There were some problems in the combustion of coal/oil/water with washing soda. In general, however, thermal efficiencies and combustion efficiency (~98%) were acceptable.

TASK 5, 6, 7.

Expected to start in October.

IV PROGRESS DETAILS

TASK 2. - BOILER, COAL FEED AND BAGHOUSE

The old boiler has been removed and the new boiler has arrived. For the installation of the new boiler, excavation of the boiler room is necessary. Once the excavation has been completed, R. B. Hamilton Hauling and Rigging Corp. have been hired to set the new boiler in place. The new boiler is presently at the

rigger's yard.

The day after the boiler is rigged into place, Stone and Webster Engineering Corp. will take on site final measurements of all the necessary connections. They have informed us that completion of the final piping and wiring prints will take one day and all the pipes and valves needed can be obtained rapidly. The estimate for completion of installation of the boiler is several weeks from the time it is in place provided contractors, pipefitters, welders and electricians are all readily available. The installation will also depend on the availability of all the materials required for complete hook up. We are presently ordering as much of the materials as possible so we can have the boiler working as soon as possible.

Stone and Webster has completed the design of the storage tank and expects to complete construction of the tank in a matter of weeks. The coal storage tank and bag house will be shipped to the rigger's yard and the riggers will transport these pieces to the Woodruff Hall boiler room at Adelphi.

TASK 3. RHEOLOGICAL ANALYSIS

While awaiting arrival of the smaller TVA coal and /or new sieve shaker, calibration and interface work was completed for the Rotovisco, Wang, and pumping tubes.

Last year, a Wang program was written to take data from the Rotovisco and calculate the viscosity of the emulsions as if they were Newtonian. In analyzing data from the pumping tubes, it became apparent that a power law model was applicable to emulsions in the region of interest, 50-150 $sec.^{-1}$ Using the power

law, precise apparent viscosities can be obtained from the Rotovisco and pumping tubes and then correlated.

The power law states:

$$T = k\,\dot{\gamma}^{n}$$

where T = shear stress
$\dot{\gamma}$ = shear rate
k = consistency index
n = non-Newtonian index

If n=1, the fluid is Newtonian and k is the Newtonian viscosity. COW (coal/oil/water emulsions) are pseudoplastic with n<1. The apparent viscosity at a given shear rate is $T/\dot{\gamma}$ which is $k\dot{\gamma}^{n-1}$. Using a power law model, Calderbank and Moo-Young [1] simplified the Krieger and Maron [2] expression for shear rate in a couette viscometer (concentric cylinder).

$$\dot{\gamma}_n = \frac{4\pi N}{1-S^{-2}}\left(1 + \frac{S^2-1}{2S^2}\left(\frac{1}{n''} - 1\right) x \left[1 + \frac{2}{3}\ln S + \frac{1}{3}\left(\frac{1}{n''} - 1\right)\ln S - \frac{1}{45}\left(\left(\frac{1}{n''} - 1\right)\ln S\right)^3\right]\right)$$

where $\dot{\gamma}$ = shear rate at given rps
N = rps (number of revolutions per second)
S = radius cup/radius bob
n'' = slope of ln torque versus ln rps curve

The Wang allows calculations of exact shear rates at various rps.

[1] Calderband, P.H., and Moo-Young, M.B., "The Prediction of Power Consumption in the agitation of Non-Newtonian Fluids", Trans. Instn. Chem Engrs., 137, 1959, p. 26.

[2] Krieger, I.M. and Maron, S.H., Journal of Applied Physics, 1954, 25,72.

7.

Because the Wang has limited memory and storage capacity, a trade-off must be made between the amount of data stored and the sophistication of the program. To overcome this difficulty, a series of eighteen programs were written thus allowing storage of fifty data points, each with two pieces of information. The electrical output of the Rotovisco is calibrated and fed into the scanner, data is usually taken every four seconds. The shear stress and shear rate, as well as the viscosity at each point are calculated as if the fluid were Newtonian and this data is graphed. The natural log of the torque and rps are calculated, stored, and graphed. Using a least square fit linear regression, the slope of the ln torque versus ln rps line, n', is found as well as the coefficient of correlation.

The slope is then used to calculate the actual shear rates at the various rps. Using the ln (shear stress) and ln shear rate and performing another linear regression, k and n are found. Besides printing these numbers out, the power law behavior of the fluid in the pipe:

$$\frac{8V}{D} = \left(\frac{4\ n}{3n\ +\ 1}\right)\ \left(\frac{1}{k}\right)^{1/n}\ T^{1/n}$$

where V = velocity

D = pipe diameter

is also calculated. Finally, the apparent viscosity using the power law shear rate is printed and plotted vs. shear rate. These programs perform a complete analysis of COW and COM using a

8.

concentric cylinder viscometer.

As was mentioned in the previous report, a ribbed rotor and stator were ordered and have now been received. This combination insures that the emulsions do not slip at the viscometer walls, causing a lowered measured viscosity. The measuring system has been calibrated and works extremely well with trial #4 oil emulsions and slurries. The spring measuring system for the torque measurements in the Rotovisco was re-calibrated and the instrument constants re-calculated.

In doing experiments on #6 COM, the ribbed rotor-stator combination worked well on concentration up to about 40%. With 50% slurries, the sample would climb up the rotor (Weissenberg effect) and overflow into the depression in the center of the rotor. This caused an improper filling of the gap. To overcome this normal stress effect, a plate and cone measuring system was installed on the Rotovisco. In this system, a small amount of sample is placed in the small gap between the flat plate and a 1^{o} cone. A spring is used to keep the plate and the point of the cone in contact, thus counteracting the normal stress effect. Because the gap is so small, special corrections do not have to be made for the shear rate and the analysis of viscosity is simplified. Using the power law, a series of Wang programs have been written to perform the same analysis as with the cocentric cylinder. This system can only be used with very viscous liquids, but is very convenient because of the small sample required.

Flush mounted diaphragm, zero to five pound, pressure transducers were installed in the small pipes used for in-pipe

viscosity measurements. These transducers use a 15 VDC power supply which was specifically constructed for use with these transducers. The output of the transducers, which is in millivolts, is fed into an amplifier and then into the Wang. A program takes the zero level reading before the test, the pressure during the test, the zero after the test, averages them and subtracts them. Each transducer has been separately calibrated and the calibration entered into the program. A thermistor is used to monitor temperature. Flow rates are measured using calibrated tubes and a stop watch. The program gives pressure, temperature, shear stress at the walls, and flow rate. Baseline oil tests are presently being performed.

TASK 4 - PARAMETRIC STUDIES OF SO_x REMOVAL ON LABORATORY BOILER

A. MODIFICATION OF THE WANG EFFICIENCY PROGRAM

Three modifications have been made in the Wang efficiency program.

(i) The MGA 1200 multiple gas analyzer has been interfaced with the Wang calculator. Voltages from the MGA are fed into the Wang. The concentration of H_2O, N_2, O_2, Ar, CO_2 and SO_2 are calculated and printed approximately every minute. These values are averaged and printed after every fuel load. Percent of excess air is then calculated by the Wang using the following equation:

$$\% \text{ Excess Air} = \frac{3.7619 \text{ concentration } O_2}{\text{Concentration } N_2 - 3.7619 \times \text{concentration } O_2} \times 100$$

(ii) The thermal efficiency in the past has been determined in two ways. The first is calculated by using the specific heat of water, the temperature difference of the inlet and outlet water, and the rate of water flow. In the second method, the energy stored in

the heat exchanger is added to the ΔT - water flow product. This stored energy is calculated by assuming a linear temperature gradient in the exchanger. Once the two results are approximately equal ($\pm 1\%$) the system is considered to be in thermal equilibrium. Thermal efficiency is then used only after the two results are within one percent.

(iii) The stack temperature is averaged and printed out after every fuel load.

B. ASH ANALYSIS

During the efficiency tests the stack sampler is used to collect a representative sample of fly ash. Knowing the total volume of gas produced during combustion and the volume of stack gas collected, the total amount of fly ash is calculated. After the test the boiler is cleaned and the ash collected from the combustion chamber, fire tubes, and top of the heat exchanger. The analysis of these samples are used in the calculation of combustion efficiency.

(i) Moisture:

A sample from each section of the furnace is analyzed for percent moisture as follows: A 0.2000 gram sample is placed in a porcelain crucible and dried at 110°C for one hour intervals until constant weight is obtained. From the loss of mass the percent moisture is calculated. The percent moisture is used in the next two procedures.

(ii) Carbon:

To figure the percent carbon retained in each sample, a dry ashing method is utilized. A 0.2000 gram sample is placed in a platinum vessel and is fused at 700°-800°C for ten minute intervals until constant weight is reached. At this time all carbon

present should be totally ashed. Percent ash and moisture contents are subtracted from 100% to give percent carbon in the ash. This percent carbon is the used in combustion efficiency calculations.

(iii) **Metals**:

The ash is tested for certain metallic elements by atomic absorption spectroscopy. Samples are prepared for analysis by fusing a 0.2 gram sample with 1.4 gram of ($LiBO_2$) in a graphite crucible at 1000°C for one hour. The bead which is formed is dissolved in 50 ml of 5 percent nitric acid. This solution is diluted to 250 ml in a volumetric flash. These samples are analyzed for the following ions: Fe, Ca, K, Mg and Na. The percent of each ion is calculated.

C. COMBUSTION EFFICIENCY

The combustion efficiency is determined using the percent unburned carbon in the ash, both that which was deposited in the furnace and the amount which was emitted as fly ash, and the percent carbon in the fuel. The assumption is made, that because of the excess air present, the percentage of carbon monoxide and hydrocarbons in the stack gas are negligible.

D. RE-CALIBRATION OF PLATINIUM RESISTANCE TEMPERATURE DETECTORS

We have found that in order to obtain an accuracy of better than a tenth of a degree celesius, the internal resistance of our measuring system must be taken into account. This was accomplished as follows:

(i) Four of the platinum resistance temperature detectors (Pt-RTD's) were calibrated by immersing the platinum thermometers

in a continuously stirred water bath whose temperature was increased at the approximate rate 0.1^{o} per minute in the range between $15^{o}C$ and $75^{o}C$. A set of calibrated glass/mercury thermometers with 0.1^{o} division was used as a reference. At one degree intervals on the mercury thermometer the Wang calculator measuring system was used to record the resistance of the thermometers (R_T) and calculate the temperatures. For abbreviated listings see Table IIA for resistance measurements and Table IB for temperature results.

(ii) Boiling points ($100.0^{o}C$) and crushed ice points ($0.1^{o}C$) were also determined.

(iii) To convert R_T to temperature the Wang was programmed to use the Callendar equation

$$T = A-B\sqrt{C-R_T}$$

where A = 3398.98, B = 131.017, and C = 773.038. These values were based on the assumption that these Pt-RTD's conformed to the standard American curve where R_0 is 100.00 ohms and R_{100} is 138.50 ohms.

(iv) The data seem to indicate that additional resistance is added to each Pt-RTD's reading by the measurement system. The actual amount depends on the channel used. See Table IIA where the experimentally determined resistances can be compared to the resistance calculated from a modified (see Note v) Callendar equation.

(v) Upon further analysis it appeared that the Pt-RTD's were not of a type that followed the standard American curve but were of a type where R_0 is 100.00 ohms but R_{100} is 139.11 ohms. (A type like this is available from Minco as type Pt 11-100.) If this is so the constants, B and C of the Callendar equation, should therefore be changed to 130 866 and 774.589. This is still being investigated.

(vi) After calculating the temperatures using the Callendar equation below the results were greatly improved as shown by comparing Table IA to IB.

$$T = 3398.96 - 130.866\sqrt{774.589 - (R_T \text{ corrected})}$$

(E) INITIAL TESTS ON LABORATORY BOILER

A total of ten combustion tests[3] were done on the laboratory boiler furnace. These results are presented in tables III and IV. The purpose of these tests were twofold:

a) To obtain baseline data on the thermal and combustion efficiency checking out the MGA multiple gas analysis and data analysis procedures.

b) Obtain some initial data on washing soda as a possible SO_x absorbent. The apparent advantage of washing soda over soda ash is its increased solubility in water. Since it is also an alkaline based compound, it should be an efficient SO_x absorbent.

(i) Baseline #6 Oil Tests:

Though our 350 HP boiler test program will mainly use #4 oil we also plan some #6 oil runs. In addition, in relation to our previous DOE contract some #6 oil runs were called for, since we were interested in performance evaluation of our redesigned burner for the #6 oil. We also present on table III a #4 oil run done before the arrival of the MGA. The heavy oil runs are also important in checking out the performance of the MGA especially SO_x since the sulfur content ($\sim$0.88%) is what we would hope to obtain after running COW with

[3]Fuel analysis is listed in appendix D

30% coal with SO_x absorbent. It is important to check the MGA in this range against a sulfur balance since Perkin Elmer does not guarantee the system below 500 ppm SO_x, although good results have been seen in lower ranges at PETC. Before the MGA is used it is calibrated with standard calibration gases in the range of interest. All calibrations indicate that the MGA can accurately measure SO_x well below 500 ppm. From Table III we see that SO_x measurements were close to the expected results using a sulfur balance. $|SO_{x\ MGA} - SO_{x\ Th}|$ are within 60 ppm in all cases and are actually identical for test 31-53. A sample calculation of $SO_{x\ Th}$ is described in appendix A. This is certainly adequate and should even improve for the more stable combustion system of the 350 HP boiler. Thermal efficiencies were good (~70%) indicating adequate combustion with our burner. For all tests, table III and table IV we estimate wall loss as $\tilde{-}$ 10%. Detailed calculations are presently being performed to find a more accurate determination of wall loss and a check for heat balance.

(ii) Coal (TVA) - Oil (#6) Slurry Tests:

The purpose of these COM tests (31-61,31-72) was to extend the results under (i) with the addition of coal for the same reasons. In addition, the increased particle loading provided a mechanism for checking our ash analysis procedure and calculating combustion efficiency. The data is presented in table IV. These two tests (31-61, 31-72) were also analyzed for certain metallic elements, the results are shown in appendix C. This initial grind of coal was relatively course (~50% thru 200 mesh). However, we had run into extreme equipment delays in obtaining the larger sieve shaker and felt that it would still

be informative to perform the combustion tests both to check SO_x and combustion efficiency with the coarse coal. The use of #6 oil was helpful in improving stability for the coarse coal grind. Combustion efficiency was 98.2% indicating good carbon burnout. (table IV) Approximately half the particulates at the top of the heat exchanger and in the stack are carbon. This would reduce our particulates by about 15% since this represents about 30% of all ash collected from the fire box, fire tubes, top of the heat exchanger and stack. We see that the predicted ash is close to that actually collected, the majority of which comes from the coal ash. The burn assumption in the combustion efficiency calculations was the CO and HC are negligible, which has shown to be the case in our previous work with the gas chromatograph. Thermal efficiencies were a few percent lower, however it would be difficult to extrapolate this from the laboratory scale to the 350 HP at this time. $\left|SO_{x\ MGA} - SO_{x\ Th}\right|$ was again within 60 ppm.

(iii) COW Emulsion Tests:

Three tests in the category are described in table IV. Test 35-16 examined a mixture of weight proportion 40 gms TVA coal (50% $\sim$ 200 mesh), 40 gms #6 oil and 10 gms H_2O. This test was done for the same reason described previously. At that time we did not have the large sieve shaker. The #6 oil was again used both as a follow up on the #6 COM tests and also due to the fact that stability was improved with coarse coal by the use of #6 oil. Thermal efficiencies were about the same as the 30-70 COM slurry. $\left|SO_{x\ MGA} - SO_{x\ Th}\right|$ is within 2 ppm for

this test run. Total particulate emissions in this test were 7.54 lb/10^6 Btu. The expected value from the coal ash is 5.49 lb/10^6 Btu. This would imply a combustion efficiency approximately 95%. It would seem that even though coarse coal was burned the SO_x emissions were relatively unaffected by the size distribution and very close to that expected under conditions of complete combustion.

Test 35 - 24 involved COW with fine ground coal (70% thru 200 mesh) and a heavy #4 oil. The sieve size of this coal is given in appendix B. The coal was made up after the new sieve shaker arrived. Though the new sieve shaker is much larger and more efficient than our original one it still takes one week to grind and prepare sufficient fine ground coal to perform a combustion test. The sieve distribution was prepared to duplicate an industrial grind similar to what we received on a similiar grade coal from Reynolds Metals and Southern Illinois University. As seen from Table IV the thermal efficiency was somewhat higher than the previous coarse coal COW test 35-29, $\left|SO_{x\ MGA} - SO_{x\ Th}\right|$ was only a few ppm. There was a somewhat better carbon burnout with this mixture. The last test, 35-29, is a combustion test with 50% stoichiometric washing soda. We experienced great difficulties in burning this mixture with satisfactory flame stability. Because of this, SO_x varied from 300 ppm to 600 ppm with an average of 450 ppm. This represents at least a 25% reduction in SO_x with possibly more since poor combustion can reduce the absorption by the alkaline. We are presently analyzing the washing soda mixture to delineate the problems with washing soda.

TABLE I

	A					B			
Temp. glass -therm.	Temp. calc. from new equation No. 1	No. 2	No. 3	No. 4		Original Temp. results No. 1	No. 2	No. 3	No. 4
0.1°C	0.12°C	0.20	0.22	0.17		1.73	0.49	0.92	1.05
15	14.87	14.92	14.94	14.92		16.54	15.25	15.70	15.85
20	19.93	19.93	19.93	19.93		21.61	20.29	20.69	20.86
25	24.90	24.95	24.95	24.93		26.58	25.33	25.73	25.87
30	29.96	29.93	29.93	29.91		31.65	30.31	30.72	30.88
35	34.94	34.97	34.97	34.97		36.66	35.36	35.77	35.94
40	39.91	39.86	39.94	39.96		41.63	40.25	40.73	40.94
45	44.96	44.94	44.96	45.01		46.69	45.36	45.78	46.00
50	50.02	50.02	49.97	49.97		51.78	50.44	50.80	50.98
55	54.88	54.86	54.88	54.91		56.66	55.30	55.73	55.94
60	59.98	60.01	60.03	59.98		61.76	60.45	60.89	61.02
65	65.11	65.06	65.09	65.04		66.92	65.53	65.97	66.09
70	70.13	70.15	70.13	-		71.95	70.62	71.00	-
75	75.15	75.09	75.12	-		76.99	75.58	76.03	-
-	-	-	-	-					
100	100.20	100.13	100.13	100.23		102.10	100.68	101.08	101.38

$$T = 3398.96 - 130.017 \sqrt{773.038 - R_T}$$

$$T = 3398.96 - 130.866 \sqrt{774.589 - R_T} \quad \text{(Corrected)}$$

TABLE II

°C	A ← OHMS					B →			
Temp. of calibrate glass therm.	(Rm) Measured resistance of Pt - RTD 's				Theor. (Rc)	Correction for each reading (Rm-Rc) Pt - RTD 's			
	No. 1	No. 2	No. 3	No. 4		No. 1	No. 2	No. 3	No. 4
-	-	-	-	-	-	-	-	-	-
15	106.53	106.03	106.20	106.26	105.94	.59	.09	.26	.32
20	108.53	108.01	108.17	108.24	107.92	.61	.09	.25	.32
25	110.49	109.99	110.15	110.21	109.89	.60	.10	.26	.32
30	112.48	111.95	112.11	112.17	111.86	.62	.09	.25	.31
35	114.44	113.93	114.09	114.16	113.82	.62	.11	.27	.34
40	116.39	115.85	116.04	116.12	115.79	.60	.06	.25	.33
45	118.37	117.84	118.01	118.10	117.74	.63	.10	.27	.36
50	120.35	119.83	119.97	120.04	119.70	.65	.13	.27	.34
55	122.25	121.72	121.89	121.97	121.66	.59	.06	.23	.31
60	124.24	123.73	123.90	123.95	123.61	.63	.12	.29	.34
65	126.24	125.70	125.87	125.92	125.56	.68	.14	.31	.36
70	128.19	127.68	127.83	-	127.50	.69	.18	.33	-
75	130.14	129.60	129.77	-	129.44	.70	.16	.33	-
-	-	-	-	-	-	-	-	-	-
100	139.83	139.28	139.44	139.55		.72	.17	.33	.44
						Ave .64	.12	.28	.34

TABLE III

Test Number	31-36	31-40	31-47	31-53	22-61
Fuel	No.6 oil	No.6 oil	No.6 oil	No.6 oil	No.4 oil
Stack temp ^0C	231.2	231.6	235.1	222.6	160
H_2O%	7.93	8.08	7.58	5.76	--
N_2%	77.4	77.4	78.2	79.2	82.2
O_2%	4.72	4.73	3.60	5.00	7.07
CO_2%	10.9	10.8	11.7	11.0	10.7
SO_2 MGA ppm	471	479	356	410	--
SO_2 Th. ppm	412	415	412	410	--
NO_x ppm	206	199	159	178	70
Excess air %	31.0	30.1	21.0	31.3	40.1
Thermal eff. %	69.7	69.2	67.7	67.2	66.0
Stack loss (dry) %	8.36	8.40	8.03	8.27	--
Water stack loss %	6.72	6.72	6.74	6.67	--
Total stack loss %	15.1	15.1	14.77	14.94	--
Soot $lb/10^6$ Btu			0.11	0.08	0.060

TABLE IV

	TVA COARSE COAL NO. 6 OIL		TVA COAL NO.4 OIL		
			COARSE	FINE	FINE WITH 50% STOICHIOMETRIC WASHING SODA
TEST #	31-61	31-72	35-16 (COW)	35-24 (COW)	35-29 (COW)
FUEL	30-70 (c/o)	30-70 c/o	40-40-10	40-40-10	40-40-10
Stack temp. °C	227.7	224.0	205.8	182.5	178.5
H_2O%	7.28	6.82	6.56	4.66	6.66
N_2%	7.73	77.7	77.6	79.4	77.3
O_2%	4.84	4.42	4.66	6.32	6.21
CO_2%	11.6	11.9	12.1	10.7	10.8
SO_2 MGA ppm	729	740	862	553	458
SO_2 Th. ppm	674	688	860	543	--
NO_x ppm	204	184	111	154	114
Excess air %	30.2	27.4	28.5	45.1	44.4
Thermal eff. %	65.1	63.3	64.5	69.4	66.2
Combustion eff. %	98.2	98.0	~95	~97	--
Inlet temp.°C	19.5	17.4	17.9	18.0	18.2
Outlet temp. °C	79.9	73.2	66.2	65.3	63.4
Water flow l/m	5.18	5.17	5.20	4.97	4.93
Stack loss (dry) %	7.81	7.53	10.1	7.76	--
Water stack loss %	6.33	6.32	6.52	6.60	--
Total stack loss %	14.1	13.8	16.6	14.4	--
Soot lb/10^6 Btu	0.73	0.25	1.32	0.88	--
Total ash deposits lb/10^6 Btu	3.09	3.19	7.54	6.78	--
Total ash predicted lb/10^6 Btu	3.10	3.10	5.49	5.49	--

APPENDIX A

SAMPLE SO_x CALCULATION

Example of SO_2 expected for 30% excess air

Content of fuel is:

Carbon = 0.8780
Hydrogen = 0.1202
Sulfur = 0.0048

Find ratio of atoms:

Carbon = 0.8780/12 = 0.07317
Hydrogen = 0.1202/1 = 0.1202
Sulfur = 0.0048/32 = 0.00015

And mole ratio:

Carbon = 0.7317/0.7317 = 1
Hydrogen = 0.1202/0.7317 = 1.643
Sulfur = 0.00015/0.7317 = 0.00205

The equation is:

$$C_1H_{1.64} + (1+0.3) \times (1+1.64/4 + 0.00205)\ O_2 + (1+0.3) \times (1+1.64/4 + 0.00205) \times (79/21)\ N_2 + 0.00205\ S$$

$$= CO_2 + 1.64/2H_2O + 0.3 \times (1+1.64/4 + 0.00205)\ O_2 + (1+0.3) \times (1+1.64/4 + 0.00205) \times (79/21)\ N_2 + 0.00205\ S$$

where 0.3 is due to 30% excess air. The total number of moles of gas is then:

moles of gas = $1+1.64/2 + 0.3 \times (1+1.64/4 + 0.00205) + (1+0.3) \times (1+1.64/4 + 0.00205) \times (79/21) + 0.00205 = 9.15$ moles

SO_2 expected in parts per million is:

SO_2 in ppm = $(0.00205/ 9.15) \times 10^6 = 224$ ppm

APPENDIX B
SIEVE ANALYSIS FOR TVA COAL FOR TESTS 35-24 AND 35-29

Composition of coal made from TVA coal P = percent of coal between the limits specified:

P > 150μ	0.35%
106μ < P < 150μ	4.60%
75μ < P < 106μ	29.95%
63μ < P < 75μ	26.75%
53μ < P < 63μ	13.25%
45μ < P < 53μ	13.45%
0μ < P < 45μ	11.65%

APPENDIX C

ASH ANALYSIS

TVA COARSE COAL NO. 6 OIL

TEST #	31-61	31-72
FUEL	30-70 (C/O)	30-70 (C/O)
Top Sample (grams)	131.2	80.6 gr.
Mg%	0.15	0.14
Fc%	0.99	4.35
Ca%	1.3×10^{-9}	Minimal
Na%	0.35	0.5
K%	0.013	2.11
Inside Sample (grams)	365.3	286.6
Mg%	0.12	0.13
Fe%	5.32	2.6
Ca%	0.08	Minimal
Na%	0.59	0.05
K%	2.43	1.30
Outside Sample (grams)	5.1	8.20
Mg%	0.15	0.14
Fe%	3.8	4.11
Ca%	5.2×10^{-3}	Minimal
Na%	0.55	.05
K%	1.75	1.73

APPENDIX D

FUEL ANALYSIS

	TVA Coal	#6 Oil	#4 Oil
Carbon %	63.64	86.55	87.29
Hydrogen %	3.89	11.39	12.50
Sulfur %	2.15	0.89	0.04
Ash %	16.6		

"COAL DESULFURIZATION DURING THE COMBUSTION OF COAL/OIL/WATER EMULSIONS: AN ECONOMIC ALTERNATIVE CLEAN LIQUID FUEL"

Interim Report for the
Period September 1, 1979 - November 15, 1979

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PREPARED FOR THE UNITED STATES
DEPARTMENT OF ENERGY

Under Contract No. DE-AC22-79PC10328

FOREWORD

This report summarizes technical progress accomplished during a 10 week period of a one year study being conducted for the Department of Energy under Contract No. DE-AC22-79PC10328. This contract has been extended to January 31, 1980. The work period was September 1, 1979 through November 15, 1979 and was accomplished under the direction of Dr. John P. Dooher, Principal Investigator. Mr. Roy Kurtzrock is the technical representative for DOE.

During this ten week period Dr. Dooher worked for 33% of his time on the project, Donald Wright 50%, Steven Jakatt 33%, Barbara Gilmartin 75%, Giro Carbone 50%, Teresa Kanabrocki 50%, a graduate assistant 50%, and a student assistant 50%.

ABSTRACT

This report represents work accomplished during a 10 week period of this project to demonstrate: "COAL DESULFURIZATION DURING THE COMBUSTION OF COAL/OIL/WATER EMULSIONS: AN ECONOMIC ALTERNATIVE CLEAN LIQUID FUEL".

The rheological and combustion properties of coal/water/oil mixtures have been investigated. In addition the use of alkaline additives to remove the sulfur oxide gases have been studied. Results on stability and pumpability indicate that mixtures of 50% by weight of coal and stoichiometric concentrations of alkaline absorbents are pumpable.

Correlation between viscometer data and pumping data follows a power law behavior for these mixtures. Thermal efficiencies are about the same as for pure oil. Combustion efficiencies are approximately 97%. It is possible to remove in a small scale combustion from 50-80% of the sulfur dioxide gases.

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I. OBJECTIVES

A) OVERALL OBJECTIVES

The overall objectives of this program are to develop the use of coal/oil/water mixtures (COW) to the point where sulfur oxides (SO_X) emissions can be controlled in a wide range of applications, such as industrial scale boilers, by simply adding alkaline absorbents to the fuel. Control of SO_X from COW is necessary if we are to implement this very promising fuel alternative to oil.

Secondary objectives of this program are to obtain sufficient data on an actual industrial scale boiler system to prove out the technical feasibility of this process.

The major thrust in this work is the removal of SO_X from stack emissions of this liquid fuel.

B) TECHNICAL OBJECTIVES

The proposed program is planned into Phase I and Phase II. Phase I will extend over a one year period. Phase II which is the second year option is planned to follow Phase I and to be an extension and detailed verification of the Phase I program.

PHASE I

1. Determine optimum economic fuel composition in terms of coal/oil/water and alkaline absorbents for the most efficient removal of sulfur oxides during the combustion of coal/oil/water

mixtures in industrial scale boilers.

2. Determine effect of SO_X absorbents on boiler thermal efficiency.

II RESEARCH TO BE PERFORMED BY CONTRACTOR

(a) The scope of work under this contract is unclassified and shall consist of developing the use of coal/oil/water mixtures (COW) to the point where sulfur oxides (SO_X) emissions can be controlled in a wide range of applications. Under Phase I of the program (lasting one year) the Contractor will determine optimum economic fuel composition in terms of coal/oil/water and alkaline absorbents for the most efficient removal of sulfur oxides during the combustion of coal/oil/water mixtures in industrial scale boilers. Also, the Contractor will determine the effect of SO_X absorbents on boiler thermal efficiency.

The effort under Phase I is composed of the following tasks:

TASK 1. Equipment order and set up: The major areas of equipment needed for data collection and analysis will be ordered and integrated.

TASK 2. Boiler, coal feed, and bag house order and installations: The large boiler, coal feed system and bag house system needed for this work will be ordered and installed.

TASK 3. Rheological Analysis: Various emulsion compositions with added alkali absorbents will be tested for flow properties and stability.

TASK 4. Parametric studies of sulfur oxides removal on laboratory boiler: Small scale laboratory studies will be done to evaluate SO_X removal for various emulsions.

TASK 5. Optimum sulfur oxides removal, fixed emulsion composition, variable alkali absorbent: One concentration of emulsion with four alkali absorbents will be tested for SO_X removal on the large boiler.

TASK 6. Optimum sulfur oxides removal for coal/oil slurry, variable alkali absorbents: Three alkali absorbents will be tested for SO_X removal in a coal/#4 oil slurry.

TASK 7. Optimization of sulfur oxides removal efficiency with emulsion composition: The composition of coal/oil/water emulsion that will give the optimum sulfur removal efficiency will be determined. This will be done for two alkali absorbents, i.e., soda ash and limestone.

(b) The scope of work shall include such other studies, investigations and services as may be mutually agreed upon.

(c) The Principal Investigator expects to devote the following approximate amount(s) of time to the contract work:

33% or 4 month or calendar year

III. PROGRESS SUMMARY

TASK 2. The boiler is in the process of being instrumented to give thermal efficiency and complete stack gas analysis.

TASK 3. The addition of SO_x removal additives are found to have a tremendous effect on the flow properties of COW.

TASK 4. Combustion efficiencies for COW are found to be approximately 97%. It is possible to remove in a small scale combustion form 50-80% of the sulfur dioxide gases.

TASK 5, 6, 7.

Expected to start before the end of November

IV. PROGRESS DETAILS

TASK 2. BOILER, COAL FEED AND BAGHOUSE

The test program on a Cleaver Brooks 350 hp fire tube boiler will demonstrate the technical feasibility of the fuel additive approach to controlling SO_x emissions from COW combustion.

To determine the effect of sulfur removal on the thermal efficiency the following procedure will be carried out. Fuel will be prepared with a Funken Mixer. Coal will be fed into the mixer

from the coal storage tank. Oil flow will be measured with a Niagara positive displacement meter water or water-additive mixtures will be measured with turbine meters going into the mixer. The fuel flow to the boiler will be measured with a Micro Motion Coriolis flow meter.

The boiler is in the process of being instrumented to give the thermal efficiency and complete stack gas analysis. In order to get accuracy of $\pm$ 1% in the thermal efficiency all important measurement will be done in duplicate. There are two platinum RTD's in both the inlet and outlet water. Two calibrated flow meters, a turbine meter and an orifice plate, will be used to measure the feedwater flow rate. Gas analysis will be done with the Perkin-Elmer Multiple Gas Analyzer for O_2, N_2, H_2O, Ar, CO_2, and SO_2. A Hewlet Packard G.C. will be used for total hydrocarbons. Particulate measurements will be made with a RAC Stack Sampler.

The target of the work is to optimize the removal of SO_x during actual operation of an industrial boiler-furnace without impairing thermal efficiency. The composition of COW emulsion that will give the best sulfur removal efficiency will be determined. This will be done for various alkali absorbents, such as, soda ash, limestone and potassium hydroxide. The effect of boiler load on sulfur removal efficiency will be determined by varying the load capacity from 50% to 100%. All tests will be for a duration of 4-6 hours. After the optimum emulsion composition, molar ratio of alkali absorbents and boiler load are determined, combustion tests of longer duration (48-72 hours) will be performed in order to verify these optimum conditions.

TASK 3. RHEOLOGICAL ANALYSIS

A. Rheological Effects of SO_x Removal Additives

For this series of rheological and combustion tests (TASK 4.), a 3.86% sulfur coal supplied to us by the TVA and ground to 74% less than 200 mesh and 52% less than 325 mesh (45 microns) and a heavy #4 oil (26 cp at 25°C) were used. The water and oil were emulsified ultrasonically and the coal stirred in. The samples were allowed to sit in a constant temperature bath until they reached 25.0°C.

Soda ash (Na_2CO_3), potassium hydroxide (KOH), and different sizes of commercial grade limestone ($CaCO_3$) were added to various compositions of coal/oil/water emulsions to determine the effect of these sulfur removal additives on viscosity and pumpability. A ribbed rotor and stator were used in the Rotovisco to prevent sample slippage. Table I presents the viscosity of emulsions at 100 seconds^{-1} without any additives. Table II is the viscosity of emulsions with water soluble additives and Table III is the viscosity of emulsions with insoluble additives mixed in with coal. The amount of additive was calculated to be 100% stoichiometric based on the sulfur content of the coal. A definite physical separation occurred in the emulsions which "broke" the Rotovisco.

From these tables it can be seen that the addition of SO_x removal additives has a tremendous effect on flow properties of COW. Past experience has shown that emulsions which separate under shear stress in the Rotovisco also separate and clog pumps, pipes and nozzles. Tests were previously conducted using the same coal

in a coarser grind, 50% through 200 mesh, and a lighter #4 oil. In this case no emulsions were stable under shear when prepared with limestone.

B. Pendulum Settling Studies

ACES uses a physical pendulum settling device to determine shifts in the center of mass upon standing for COM and COW. In order to gain an insight into what these shifts actually mean in terms of storage requirements, a large settling column has been constructed from which samples can be withdrawn.

It was found that viscosity is very sensistive to changes in coal concentration in coal/oil slurries, so it is a good indicator of the amount of settling. For this test, a 50% coal in heavy #4 oil slurry was prepared and placed in the settling column, Rotovisco, and the pendulum tube. Data was taken immediately upon preparation, after one hour, two hours, 4.75 hours and one day. After one day, the slurry was difficult to remove from the column, and broke at high shear rates in the Rotovisco. In Figure 1, the percentage shift in viscosity at 66 seconds $^{-1}$ is plotted against the percentage shift of the center of mass. In one day the viscosity went from 850 cp to 5700 cp while the center of mass shifted 0.24 cm out of a total length of 17 cm. Tests are presently being conducted on a slower settling slurry so that data can be collected over a longer period of time.

TASK 4. PARAMETRIC STUDIES OF SO_x REMOVAL ON LABORATORY BOILER

A. Instrumentations

Our laboratory boiler is instrumented with platinum

resistance thermometers, thermocouples, flow meters and gas analysis equipment. We have updated the instrumentation of our laboratory boiler by interfacing our Wang calcualator with the MGA 1200 Multiple Gas Analyzer from Perkin-Elmer. The output voltages from the MGA are fed into the Wang. The concentrations of H_2O, N_2, O_2, Ar, CO_2 and SO_2 are printed approximately every minute. These values are averaged and printed after every fuel load. The percent of excess air is then calculated by the Wang using the following equation:

$$\text{Excess air } (\%) = 100X \frac{O_2}{\frac{21}{79} N_2 - O_2} \quad (1)$$

B. Combustion Efficiency Calculation

The combustion efficiency is determined using the percent of unburned carbon in the ash, both that which was deposited in the furnace and the amount which emitted as fly ash, and the percent carbon in the fuel. The assumption is made, that because of the excess air levels used, the concentrations of carbon monoxide and hydrocarbons in the stack gas are negligible. Combusiton efficiencies are found to be approximately 97% for the various mixtures of COW. Combustion efficiencies for various tests are listed in Table IV.

C. Thermal Efficiency Calculation

Before each test the heat content of the fuel is entered into the Wang Calculator. The weight of the fuel is entered

manually after every fuel load burn. Thermal efficiency is determined in two ways. The first is calculated by using the specific heat of water, the temperature difference of the inlet and outlet water, and the rate of water flow. The thermal efficiency is then computed as:

$$\text{Thermal eff.} = S_w W_f \Delta T / H_f A_f \qquad (2)$$

where S_w = specific heat of water

W_f = total water flow

H_f = heat content of the fuel

A_f = weight of a batch of fuel

and

$$\Delta T = T_{out} - T_{in} \qquad (3)$$

where T_{out} = average outlet temperature over the fuel load

T_{in} = average inlet temperature over the fuel load

In the second method, the energy stored in the heat exchanger is added to the ΔT - water flow product. This stored energy is calculated by assuming a linear temperature gradient in the heat exchanger. Once the two results are approximately equal ($\pm$ 1%), the system is considered to be in thermal equilibrium and the efficiency calculated by Equation 2 is used in the average thermal efficiency.

D. SO_x Removal

The results presented in Table IV show SO_2 removal in a laboratory scale boiler. The sieve distribution, sulfur content of the coal, and percent stoichiometric of SO_2 removal additives are the same as that for the rheological tests in TASK 3, with

the exception of test no. 4. For test no. 4 a lower sulfur coal (2.15%) was used and the size distribution was a standard industrial grind.

Test no. 1 and 2 are with #4 oil. The purpose of presenting #4 oil tests is twofold: (i) To obtain baseline data on thermal and combustion efficiency and (ii) to check out the MGA. It is important to check SO_2 measured by the MGA, $SO_{2\ MGA}$, against theoretical SO_2 calculated, $SO_{2\ TH}$, since Perkin-Elmer does not guarantee the system below 500 ppm SO_2, although good results have been seen in the lower ranges at PETC. Before the MGA is used, it is calibrated with standard calibration gases in the range of interest. All calibrations indicate that the MGA can accurately measure SO_2 well below 500 ppm. For tests no.1 and 2 we see that $SO_{2\ MGA}$ is close to the expected $SO_{2\ TH}$.

Test no. 3 is a 40-40-10 COW mixture (40 gms TVA coal, 40 gms #4 oil and 10 gms water). For test no. 3 there were no additives for the removal of SO_x. The importance of this test is that one can compare it against tests with SO_x absorbents, and check for a sulfur balance.

Test no. 4 is a 40-40-10 mixture of COW with Na_2CO_3. For test no. 4 SO_2 was calculated to be 481 ppm and the SO_2 measured by the MGA was 239 ppm, corresponding to a 50% reduction in SO_2. For test no. 5, 40-40-15 COW with Na_2CO_3, the SO_2 reduction was 55%.

Test no. 6 and 7 are a 40-40-5 and a 40-44-5 mixture, each with KOH. Test no 6 shows a 84% reduction in SO_2 and test no. 7 shows a 72% reduction.

The last test, no. 8 is a 40-40-5 mixture with $CaCO_3$. The SO_2 reduction for this test was found to be 39%.

TABLE I

VISCOSITY OF EMULSIONS WITHOUT ADDITIVES

grams coal	grams oil	grams water	grams additives	η_{100} centipoise (± 3%)
40	40	5	0	933
40	40	10	0	942
40	40	15	0	1289
40	40	20	0	1600

TABLE II

VISCOSITY OF EMULSIONS WITH WATER SOLUBLE ADDITIVES

grams coal	grams oil	grams water	grams additives	η_{100} centipoise ($\pm$ 3%)
40	40	5	soda ash	*
40	40	10	soda ash	*
40	40	15	5.1g soda ash	1037
40	40	20	5.1g soda ash	broke 295 $sec.^{-1}$
40	40	5	5.4g potassium hydroxide	1092
40	40	10	5.4g potassium hydroxide	1111
40	40	15	5.4g potassium hydroxide	broke 377 sec^{-1}
40	40	20	5.4g potassium hydroxide	broke 328 sec^{-1}

*5.1 grams of Na_2CO_3 cannot be dissolved in 5 or 10 grams of water.

TABLE III

VISCOSITY OF EMULSIONS WITH INSOLUBLE ADDITIVES - MIXED IN WITH COAL

grams coal	grams oil	grams water	grams additives	η_{100} centipoise ($\pm$ 3%)
40	40	5	4.8g limestone p<45μ	1356
40	40	10	4.8g limestone p<45μ	1431
40	40	15	4.8g limestone p<45μ	broke 361 sec^{-1}
40	40	20	4.8g limestone p<45μ	unstable emulsion
40	40	5	4.8g limestone p<53μ	1074
40	40	10	4.8g limestone p<53μ	broke 505 sec^{-1}
40	40	15	4.8g limestone p<53μ	broke 659 sec^{-1}
40	40	20	4.8g limestone p<53μ	broke 230 sec^{-1}

TABLE III

(Continued)

grams coal	grams oil	grams water	grams additives	η_{100} centipoise ($\pm$ 3%)
40	40	5	4.3g limestone p<75μ	1187
40	40	10	4.8g limestone p<75μ	broke 581 sec^{-1}
40	40	15	4.8g limestone p<75μ	unstable emulsion
40	40	20	4.8g limestone p<75μ	unstable emulsion

TABLE IV

TEST RESULTS ON LABORATORY BOILER

Test No.	1	2	3	4	5	6	7	8
Fuel	#4 oil	#4 oil	40-40-10	40-40-10	40-40-15	40-40-5	40-44-5	40-40-5
Additive	------	------	--------	Na_2CO_3	Na_2CO_3	KOH	KOH	$CaCO_3$
Combustion efficiency %	99.5	99.7	94.2	97.8	98.4	96.0	98.4	96.5
Thermal efficiency %	66.8	67.6	61.9	61.9	68.3	----	68.4	63.2
SO_2 MGA ppm	146	158	944	239	453	175	284	656
SO_2 TH ppm	152	150	1098	481	1004	1118	1030	1069
% Reduction in SO_2	----	----	-----	50	55	84	72	39

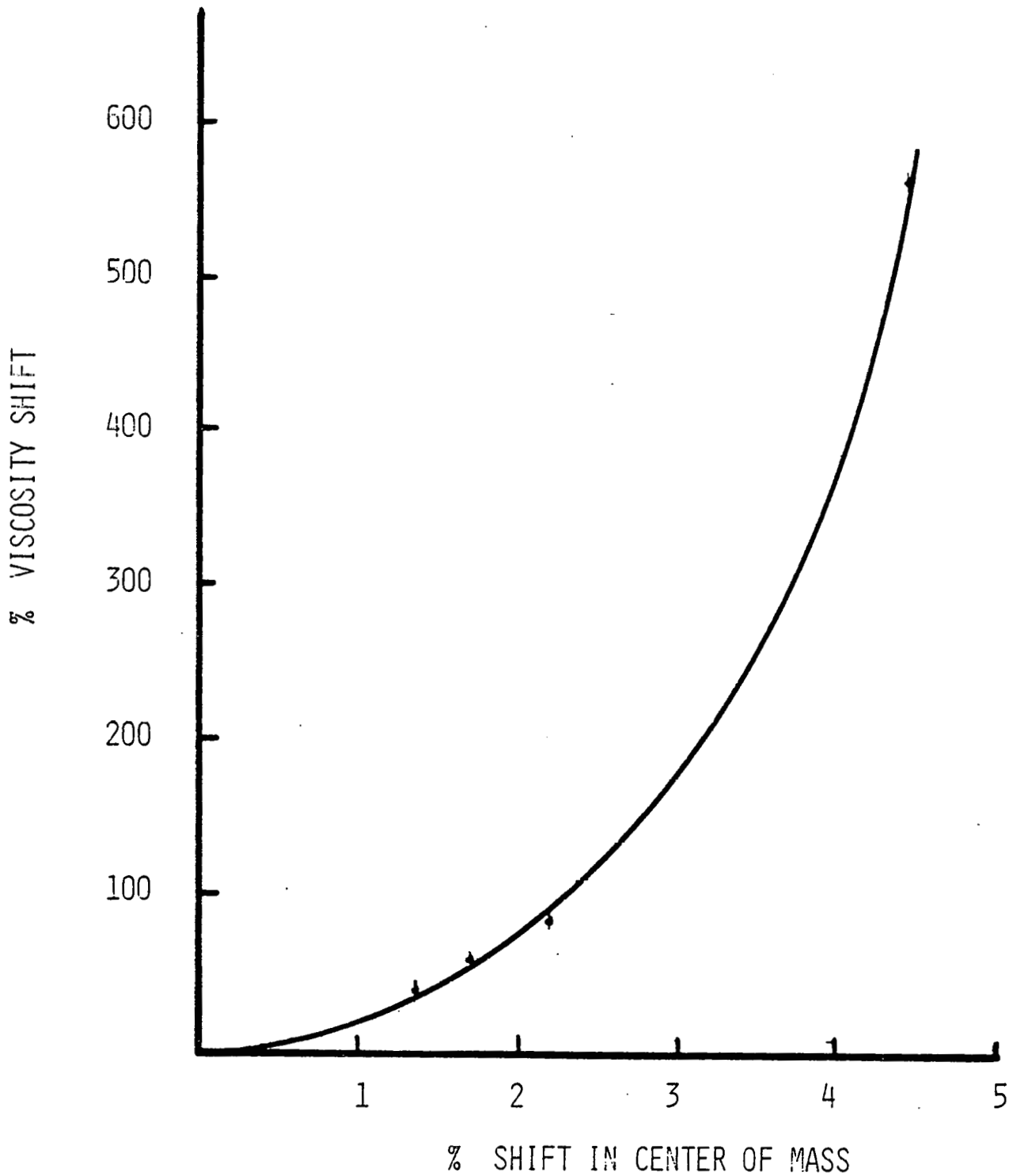

FIG. 1 PERCENT SHIFT IN VISCOSITY VS. PERCENT SHIFT IN CENTER OF MASS