

TITLE: DOE SAMPLE BANK COALS FOR LIQUEFACTION RESEARCH

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Objective:

An ongoing objective of our project "Establishment and Maintenance of a Coal Sample Bank and Data Base" has been to provide coals from a well-maintained and well-characterized suite of 54 for use by DOE researchers and contractors, with special emphasis on the needs of those involved in liquefaction research. Specific objectives have been to investigate the extent to which a new storage method prevents the deterioration of coal properties including liquefaction behavior, and the selection of a coal suitable as a standard for dispersed catalyst testing.

Accomplishments and Conclusions:

Comparative Studies of Coal Storage Methods

In the Penn State Coal Sample Bank (1,2), field collection and bulk sample storage were previously accomplished with 113 L polyethylene barrels (100 kg capacity) and 19 L buckets (16 kg capacity), both fitted with gasketed lids and valves for argon introduction. Smaller splits of samples at -0.85 mm have been stored in heat-sealed argon-filled polyethylene bags sealed in standard #2 steel cans (600 mL, 400 g capacity).

More recently, coals have been stored in laminated foil and plastic bags which are constructed of three layers; polyethylene inside allows heat-sealing and shields the contents from the middle aluminum foil layer which provides a barrier to gas transport and light. An outer spun-bonded polyethylene layer resists tears and abrasion. Sealing may be accomplished by manual flushing with inert gas and a manually operated sealer, or an automated vacuum/inert gas sealer as used in the food industry. An earlier report (3) demonstrated that the foil bags maintained an inert atmosphere and preserved coal quality better than the other container types. In current practice, steel barrels with high-density gaskets are employed for field collection and temporary storage prior to processing. Samples are processed into -6 mm and -0.85 mm mesh sizes. Coal crushed to -0.85 mm is stored as 300 g splits in 19 x 24 cm foil laminate bags; -6 mm material is stored in either 2 kg or 12 kg splits in larger bags (23 x 38 or 50 x 64 cm). In the present report, the results of further studies into the

preservation of the quality of coal stored in different types of containers are described.

Oxygen levels in the containers' internal atmospheres were measured with a polarographic oxygen detector (Fig. 1). Low oxygen levels in the foil bags and cans are assumed to be the principal reason for better preservation of coal samples in these containers.

Figure 2 is a plot of initial calorific value (dry) against values obtained after storage at -6 °C in the polyethylene drums over 68 months. The regression lines show a clear shift to lower calorific values for the three sets of repeat analyses; after approximately 3 years the average decrease in calorific value was about 130 Btu/lb, whereas after approximately 5½ years the decrease had become 300-400 Btu/lb.

Splits of 53 of the DOE coals of varying rank stored in barrels and cans were monitored for other evidence of deterioration.

Gieseler fluidity, sulfate sulfur and calorific value changed during storage over a period of four years. In the graph of Gieseler fluid range (Fig. 3), lower values after storage indicate oxidation or deterioration of the sample. In the graph of sulfate sulfur (Fig. 4), higher values after storage indicate oxidation of pyritic sulfur to sulfate. Both graphs show that splits stored in cans were better preserved than those in barrels, and that deterioration increases with time. A related study showed buckets to be similar to barrels in their preservation ability.

The initial results of a study planned to measure changes in several properties through time for a coal sample stored in different container types including the foil laminate bags were described earlier (3). Further results of this study can now be reported. Because fluidity had changed significantly during storage in previous studies, a coal with fluidity was desired for this study. A run-of-mine sample of medium volatile (mean-max R 1.27%) Lower Kittanning seam coal was collected in western Pennsylvania. The sample was immediately taken to Penn State, crushed, split and prepared for analysis. Gieseler fluidity, free-swelling index and alkali extraction results were obtained within 30 hours of the coal being mined. Epoxy-binder pellets for fluorescence microscopy and splits for other analyses were also prepared at this time.

Splits of the sample were packaged in several container types for the study: -6 °C coal in polyethylene buckets and foil laminate bags; -0.85 °C coal in steel cans, foil laminate bags and an open container exposed to the atmosphere. After 4, 16, 52, 93 and 116 weeks containers were opened and samples analyzed as had been done for the original sample.

Fluid properties (Gieseler plasticity and free-swelling index) are among the most sensitive indicators of deterioration during storage. The fresh Lower Kittanning sample had a maximum fluidity of 1224 ddp_m with a

fluid range of 100°C. Figure 5 shows that foil laminate bags maintain fluid range better than steel cans and much better than buckets. After storage for 52 weeks, the sample stored in the bucket had lost its thermoplastic character. However, the fluid range of the bagged -0.85 mm coal had dropped only to 95°C. Maximum fluidity and free-swelling index showed similar trends.

Another sensitive indicator of deterioration, particularly in coals with abundant iron sulfide minerals, is the oxidation of sulfides to sulfates. Figure 6 shows that foil laminate bags avoid production of sulfates better than cans and much better than buckets. As with fluid range, the bucket sample was even worse than the sample exposed to the atmosphere. The bucket sample had much higher moisture than the exposed sample, perhaps caused by leakage, trapping of moist air, and subsequent condensation. Surface moisture would accelerate the sulfide to sulfate reaction. The sulfate sulfur values of the initial sample, the final bagged sample (-0.85 mm) and the final exposed sample were 0.06, 0.04 and 1.09%, respectively.

Figure 7 shows the change over time of the alkali transmittance test (4), carbon content, and calorific value of the mvb sample over time of storage in foil bags as opposed to a sample left exposed to the laboratory atmosphere. From an initial alkali transmittance value of 100%, the exposed sample gave a value of 93% after 116 weeks whereas the sample stored in foil bags at -0.85 mm gave a value of 97.1%. From an initial carbon content of 84.6% the exposed sample had dropped to a low of 80.6% whereas the bagged sample gave a value of 84.1%. The calorific values of the original, bagged and exposed samples were 15340, 15350 and 14610, respectively.

Argonne National Laboratory's Premium Coal Sample Program supplies coal samples in flame-sealed, nitrogen-filled glass ampoules (5). Ten ampoules of each of the six available bituminous coals were obtained. Two of each were opened and analyzed to obtain initial Gieseler fluidity and alkali extraction values. Four of each were placed in a nitrogen-filled glovebox where they were opened and the contents resealed in foil laminate bags. Four of each remained unopened. After eight months and two years analyses comparing the coal resealed in foil laminate bags with that in the undisturbed ampoules were performed.

For the Argonne premium samples, Figure 8 shows that samples repackaged in foil laminate bags and stored for two years compared well to those stored in their original ampoules. After two years, maximum fluidities of these pairs of samples matched within experimental error for all except ANL-701. Fluid ranges matched within experimental error for all except ANL-501 and -701. The variation in results for ANL-701 is probably caused by problems with the Gieseler plastometer. Dashed lines on the graphs for ANL-301, -401 and -601 indicate that the 8-month test could not

be successfully completed on the amount of coal allocated because multiple repeat runs were required to meet the ASTM precision requirement.

Based upon the studies described above and the desire to improve sample preservation in long-term storage, samples collected since December, 1989 are being stored in foil laminate bags after processing. At this time all such samples are designated DECS (Department of Energy Coal Samples).

Liquefaction Behavior of Stored Coal

In a previous report (3), the effect of storage on liquefaction of a medium volatile bituminous coal (PSOC-1536) was described. Because a high volatile bituminous coal would be more suitable and informative for this kind of testing, the Pittsburgh seam (DECS-12; hvAb) was tested for liquefaction performance while fresh. Subsamples were stored in foil bags and exposed to the atmosphere at laboratory conditions. Testing was repeated on these subsamples after 26 weeks. The conditions of hydrogenation (Table 1) were selected not to optimize conversion, but to emphasize minor compositional differences in the products derived from the two stored samples. Table 2 shows that whereas the liquefaction response of the sample stored in the foil bag had not deteriorated, there was a small but significant decrease in conversion of the exposed coal.

Selection of a "Standard" Coal for Dispersed Liquefaction Catalyst Testing

A current goal of PETC is to use a single coal for testing the comparative behaviors of dispersed catalysts. The criteria for selecting the coal were 1) a high volatile bituminous rank, 2) high vitrinite content, 3) low pyritic sulfur, 4) low iron, and 5) low ash. A low iron content was specified in order to avoid the catalytic activity of pyrite which is a feature of the Illinois #6. The Blind Canyon seam, Utah was selected as the best candidate from among several considered. Table 3 gives some pertinent information for this coal, DECS-17, which was collected on August 5, 1991.

In order to examine the liquefaction behavior of this coal relative to that of the Illinois #6, both PETC and Sandia laboratories performed comparative testing on DECS-16, a recent but earlier sample of the Blind Canyon seam. Table 4 lists the testing protocols followed by these two labs; the results of the hydrogenations are given in Table 5. It was judged that DECS-16, although giving conversion and yield values somewhat lower than the Illinois #6, performed very well. DECS-16 was not selected as the standard coal because of its rather high ash (13.9%).

Plans:

Multiple splits of standard sample DECS-17 are immediately available on request. It is planned to provide this coal in subsamples of approximately 35 g at -60 mesh in batches of 8 foil pouches. All samples

of this coal and proportions of other DECS samples will be stored under refrigeration at 3°C.

Plans are under way for the collection of 5 samples to replace depleted or deteriorated coals. By April, 1992 there will be 22 DECS samples stored entirely in foil bags.

References:

1. Glick, D.C. and A. Davis, 1991, Operation and Composition of the Penn State Coal Sample Bank and Data Base, *Org. Geochem.*, v. 17, p. 421-430.
2. Penn State Energy and Fuels Research Center, 1990, *The Penn State Coal Sample Bank and Data Base*, 2nd ed., 61 pp.
3. Davis, A., D.C. Glick and G.D. Mitchell, 1989, The DOE Coal Sample Bank -- Monitoring of Coal Deterioration, *Proc. Direct Liquefaction Contractors' Review Meeting*, Pittsburgh, PA, p. 211-222.
4. Lowenhaupt, D.E. and R.J. Gray, 1980, The Alkali-Extraction test as a Reliable Method of Detecting Oxidized Metallurgical Coal, *Int. J. Coal Geol.*, v. 1, p. 63-73.
5. Vorres, K.S., 1990, The Argonne Premium Coal Sample Program, *Energy & Fuels*, v. 4, p. 420-426.

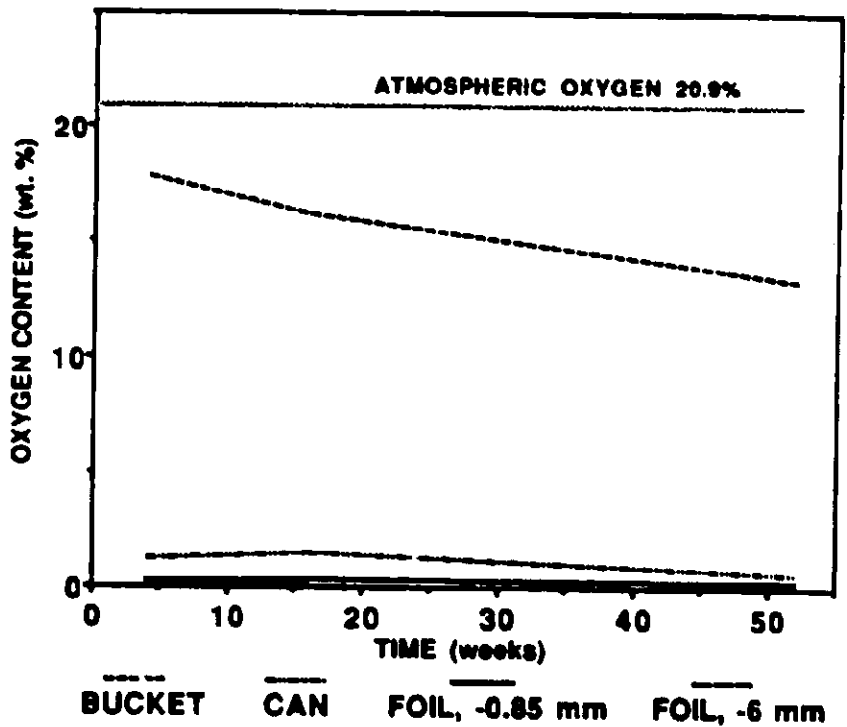


Figure 1. Oxygen in Container Atmospheres, mvb Lower Kittanning Seam Sample

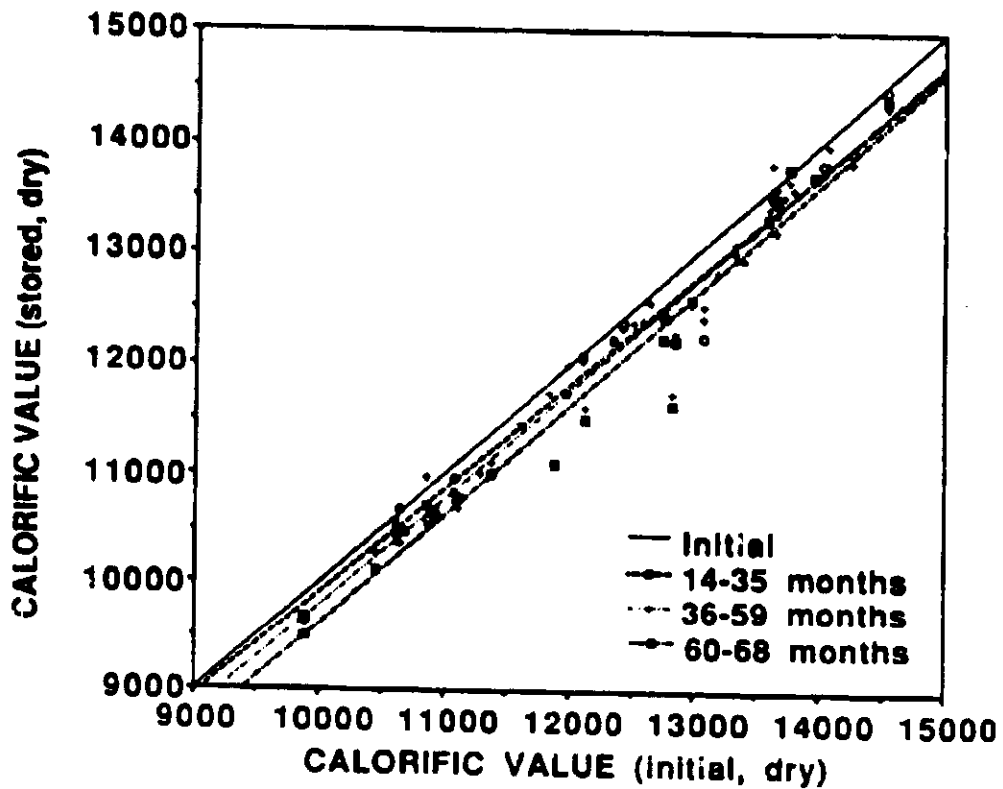


Figure 2. Calorific Value: Linear Regression on 53 Samples, -1/4" Coal Stored in Polyethylene Drums

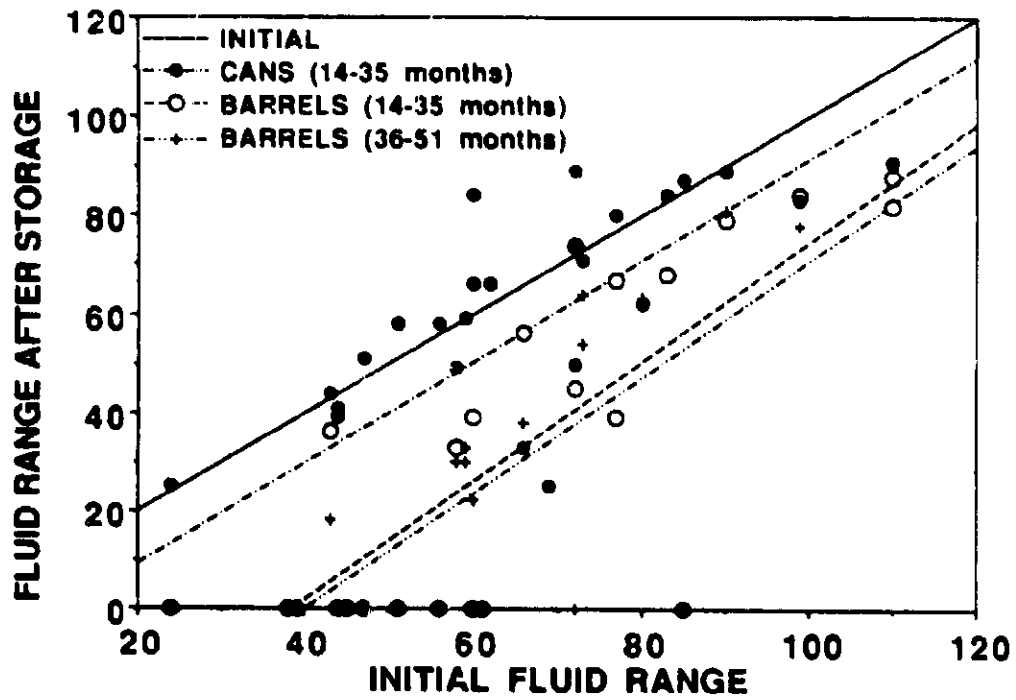


Figure 3. Gieseler Fluid Range (°C), Linear Regression on 28 Bituminous Samples

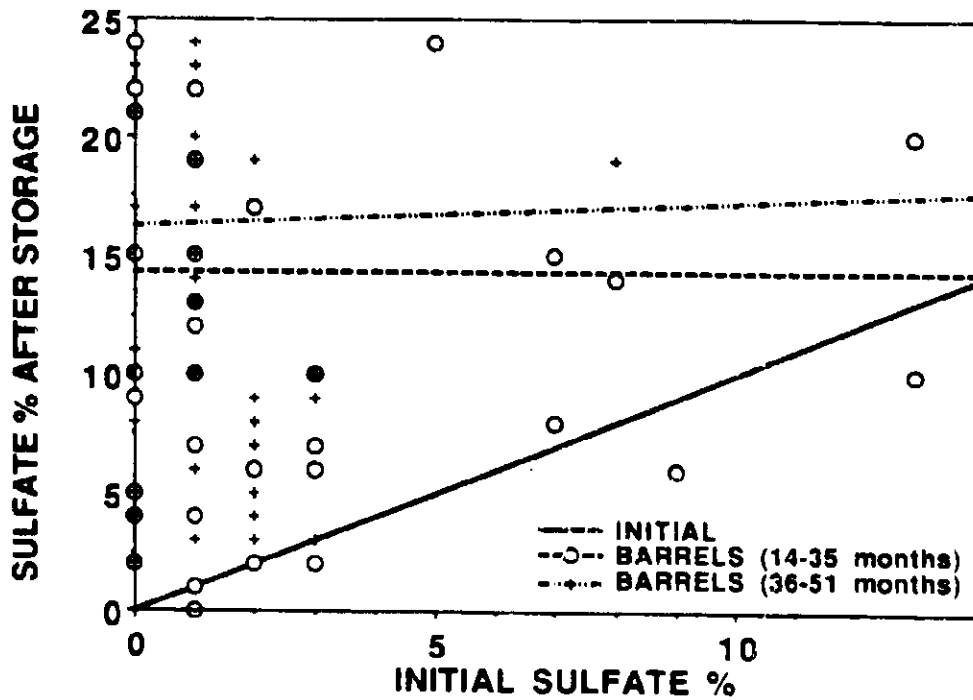


Figure 4. Sulfate Sulfur as Percent of Total Sulfur, Linear Regression on 53 Samples

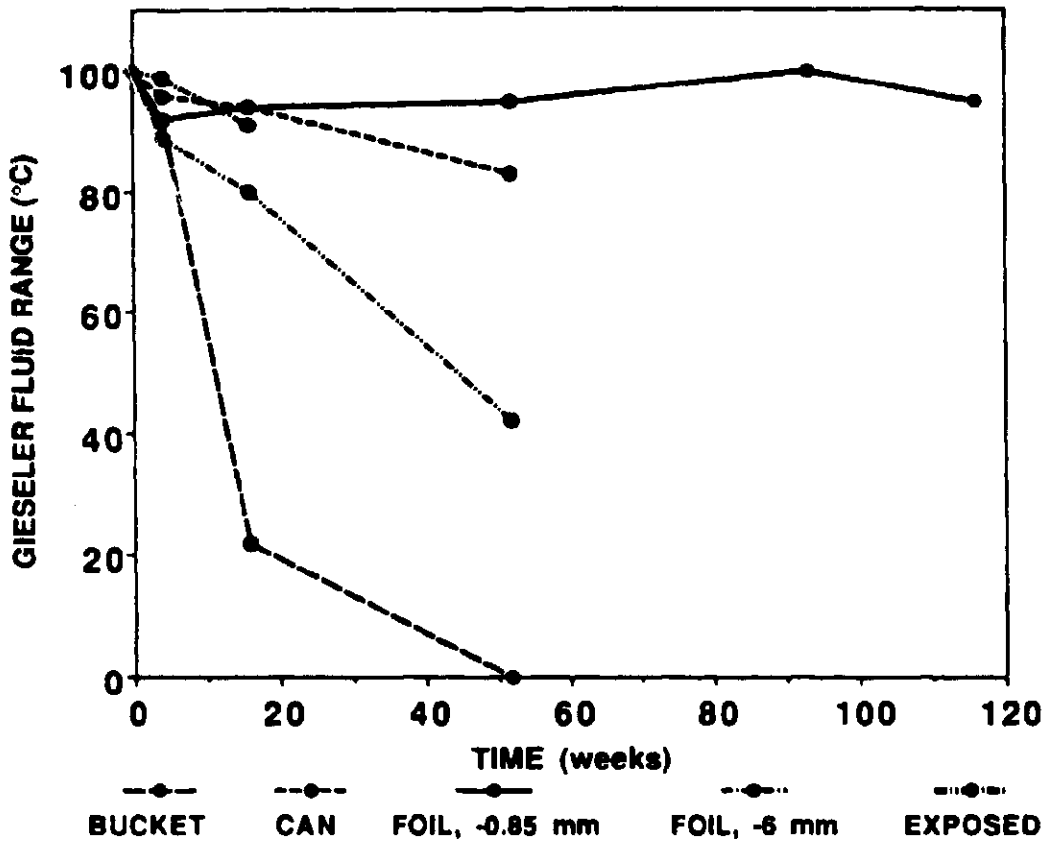


Figure 5. Gieseler Fluid Range of mvb Lower Kittanning Seam Sample

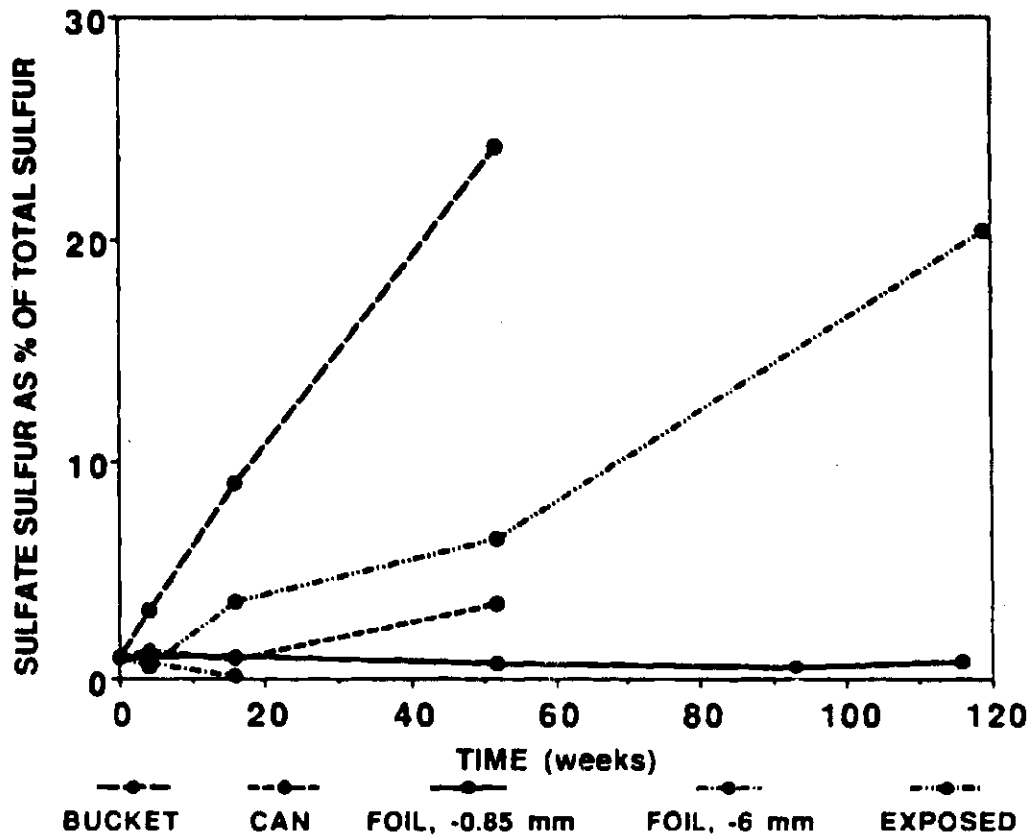


Figure 6. Sulfate Sulfur as Percent of Total Sulfur, mvb Lower Kittanning Seam Sample

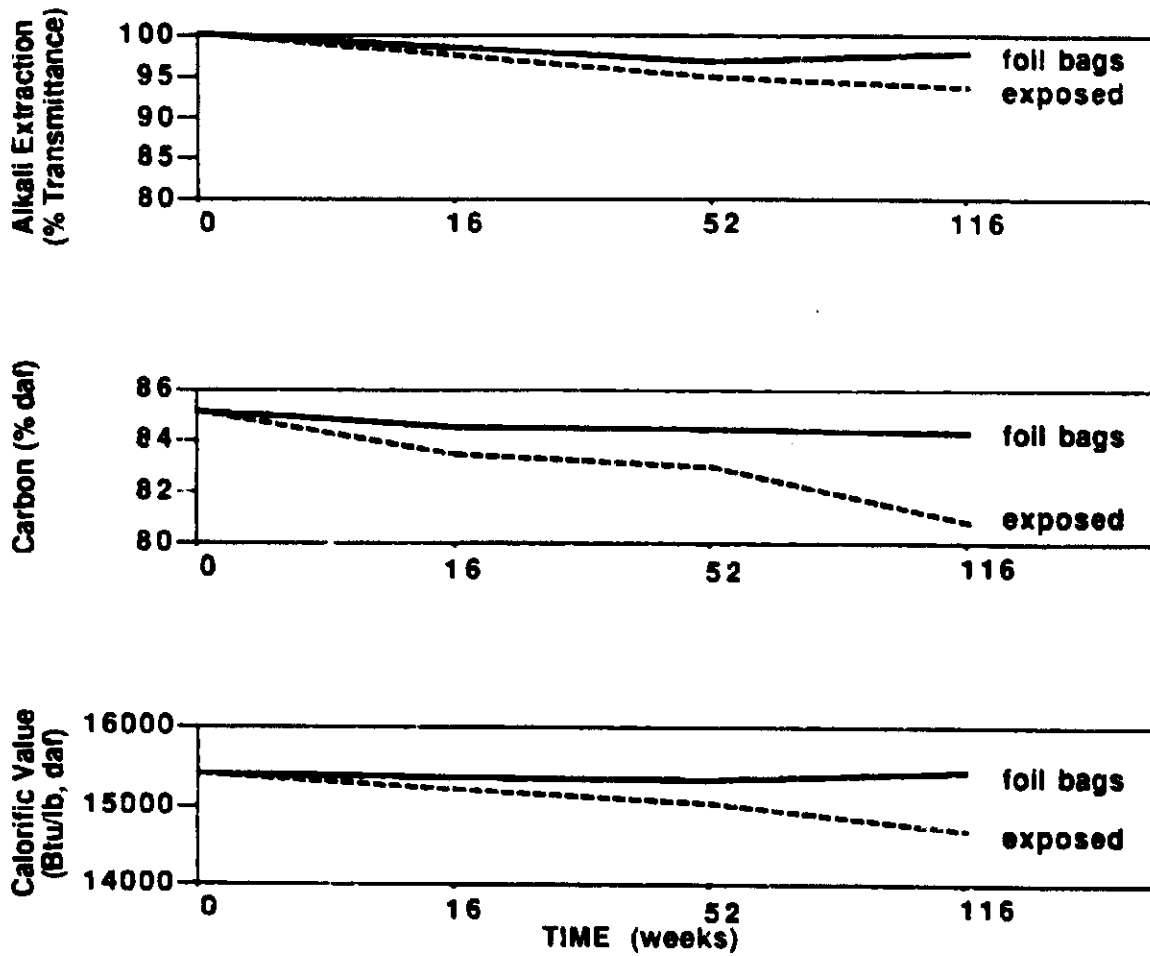


Figure 7. Changes over Time by Storage Method, mvb Lower Kittanning Seam Sample

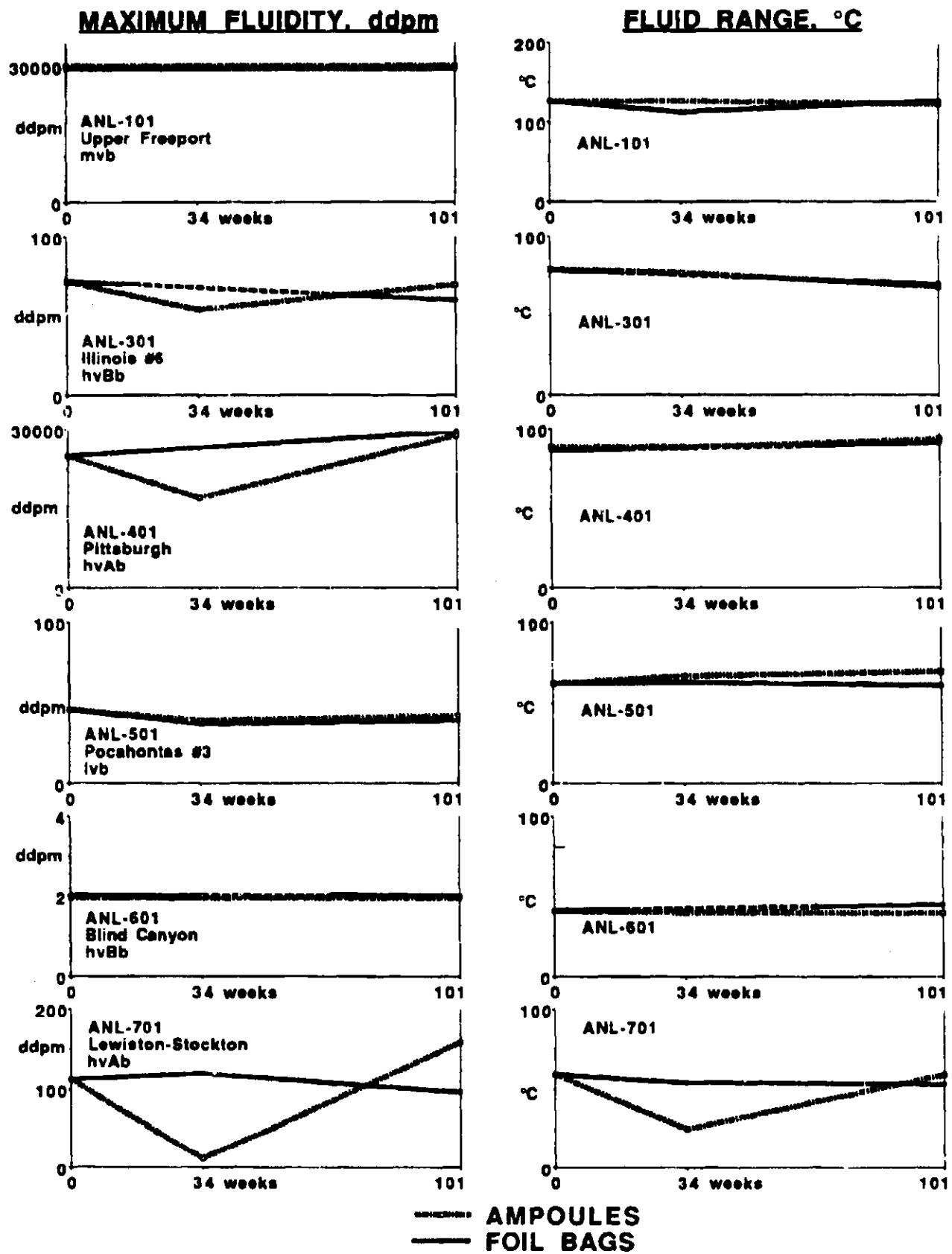


Figure 8. Changes in Gieseler Fluidity over Time, Argonne National Laboratory Bituminous Coal Samples Stored in Foil Bags and Original Ampoules

Table 1. Liquefaction Run Conditions for Penn State Test

Temperature:	350°C
Time:	30 min.
Atmosphere:	H₂
Pressure:	1000 psig
Solvent:	Tetralin
Solvent / Coal Ratio:	2 : 1

Table 2. Liquefaction Data from Penn State Test on DECS-12 (Pittsburgh Seam)

	Initial	Exposed 24 Weeks	Foil Bag 26 Weeks
% Conversion	43.1 ± 0.6	40.5	45.3
% Asphaltenes	41.2 ± 0.7	42.5	41.7
% Oil + Gas	1.9 ± 0.9	-2.0	3.6

**Table 3. Data for DECS-17, Blind Canyon Seam,
Emery County, UT**

Rank : high volatile B bituminous			
Collected : 8/5/91			
Age : Upper Cretaceous			
Formation : Blackhawk			
Seam Thickness : 8 ft. 4 in.			
Sample Thickness : 5 ft.			
	<u>Proximate</u>	<u>Ultimate</u>	
	a.r., %	% d.a.f.	
Moisture	3.7	C 81.6	Pyritic 0.02
Ash	6.3	H 6.2	Sulfatic 0.01
V.M.	45.0	N 1.4	Organic <u>0.41</u>
			Total 0.44
			0.36
	<u>Reflectance 0.59%</u>		
<u>Maceral Vol. %, min.-free (white + blue light)</u>			
	Total Vitrinite	Total Liptinite	Total Inertinite
	79.7	12.2	8.1
<u>Alkali Extraction Test</u>			
	Transmittance : 86%		

Table 4. Liquefaction Run Conditions for PETC and Sandia Tests

	PETC Test	Sandia Test
Temperature:	425°C	375, 400°C
Time:	60 min.	30 min.
Atmosphere:	H ₂ /3% H ₂ S	H ₂
Pressure:	2000 psi	1350 psi
Solvent:	?	HHP
Catalyst:	1100 ppm Mo	Shell 324

Table 5. Liquefaction Data from DECS-16 (Blind Canyon Seam)

PETC Test			Sandia Test				
	DECS-16	III #6		375°C		400°C	
				DECS-16	III #6	DECS-16	III #6
THF-sol	88.3	89.6	THF-sol	86.7	96.1	94.0	96.1
Cyclo-hexane-sol	56.9	61.7	Heptane-sol	25.6	37.0	43.3	53.8