

## MONITORING THE OXIDATION OF COALS IN STORAGE

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### ABSTRACT

Two studies of conventional coal sample storage containers revealed problems with the atmospheric gas composition and preservation of the samples. Heat-sealable polyethylene/aluminum foil laminate bags were evaluated by various methods in two further studies. The first compared preservation of a freshly collected mvb coal in laminate bags to other container types. The second compared Argonne premium coal samples sealed in their original ampoules to those repackaged in laminate bags. Preservation in laminate bags is better than in conventional containers and comparable to glass ampoules. Samples collected after 1988 for the Penn State Coal Sample Bank have been stored exclusively in laminate bags after processing. Monitoring the condition of these samples is an ongoing project.

### INTRODUCTION

When coals are stored in a sample bank for use over a period of months or years, it is important to preserve their original properties. If preservation is not achieved, measurements made after the passage of time will not be comparable to those obtained from the fresh sample. Among the properties which may change are pyritic and sulfate sulfur content, calorific value, thermoplastic properties as measured by free-swelling index and the Gieseler plastometer, fluorescence, FTIR spectra, liquefaction yields and products, alkali extraction and methane content. Some changes are purely chemical, many involving oxidation. Others may have a physical component related to relaxation after release of lithostatic pressure in mining and comminution in sample preparation.

### STUDIES OF CONVENTIONAL CONTAINERS

The environment of a coal sample in storage differs greatly from its in situ environment prior to mining. Conventional laboratory and bulk materials containers such as barrels, buckets, cans, jars and bags are typically used for storage. The internal atmosphere is often replaced with nitrogen or argon to reduce oxidation.

In the Penn State Coal Sample Bank (1), 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).

The composition of the atmospheres within barrels and buckets over time was studied using gas chromatography. Different methods of argon introduction were used on three containers of each type:

for 113 L barrels:

- 1) The lid was sealed, and the container was pumped with a small vacuum pump for approximately 2 minutes, then argon was introduced until a slight positive pressure was reached.
- 2) Same, except with large vacuum pump.
- 3) The lid was placed loosely over the container to allow the introduction of a stainless steel wand, through which argon was introduced to the bottom of the container. The wand was gradually withdrawn while the argon flowed for approximately 4 minutes, and the lid was sealed.

for 19 L buckets:

- 1) The lid was sealed, and the container pumped with a small vacuum pump for approximately 30 seconds, until the bucket began to deform. Argon was introduced until a slight positive pressure was reached.
- 2) Same, except that the pumping and argon introduction were repeated after 3 hours.
- 3) A wand was used as in #3, under barrels, above.

The results of monitoring the atmospheric compositions (Fig. 1) showed that some argon introduction methods were more effective but all containers tended to leak so that after one month the argon had escaped.

In another study, splits of 53 coals of varying rank stored in barrels and cans were monitored. Gieseler fluidity, sulfate sulfur and calorific value changed during storage over a period of four years. In the graph of Gieseler fluid range (Fig. 2), lower values after storage indicate oxidation or deterioration of the sample. In the graph of sulfate sulfur (Fig. 3), 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.

After initial processing, each of the 53 coals occupied two full barrels (at -25 mm particle size) and one half-full barrel (at -6 mm). Polarographic oxygen analysis was performed on one barrel of each particle size for each coal. Two trends were observed in the results (2). Gaseous oxygen levels in the drums were related to coal rank, with low oxygen values for most low-rank and high-volatile bituminous coals and high values (above 15%) for all medium- and low-volatile bituminous and anthracite coals. This is interpreted as better scavenging of oxygen by low-rank coals. The half-full drums also had higher oxygen levels than the full drums. The coals stored in barrels at -6 mm showed an average decrease in calorific value of only 130 BTU/lb (dry, ash-free basis) (2).

For the bituminous coal samples stored in cans, alkali extraction values (3) were plotted against decrease in Gieseler fluid temperature range (4). For bituminous coals, alkali extraction is a measure of the state of weathering at the time of collection, whereas Gieseler fluidity parameters are sensitive indicators of deterioration during storage. Decreases in fluid temperature range varied from zero to 60°C, with more than half decreasing less than 10°C, while alkali extract transmission of nearly all samples was above 94%. Thus many of the samples stored in cans were judged to be preserved rather well, while a few had deteriorated noticeably.

Although some changes in storage are probably inevitable, it was concluded that the degree of preservation achieved in polyethylene pails and barrels was unsatisfactory. The difference in preservation between cans and larger containers was also considered a problem. When the initial stock of cans of a given sample was depleted, a new batch of cans made from the contents of a bucket would be more deteriorated. Other container types which would better preserve coal samples of varying amounts were sought.

#### **FOIL/POLYETHYLENE MULTILAMINATE BAGS**

A study by Sharp (5) reported the use of laminated foil and plastic bags to preserve moisture and calorific value. These bags 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.

#### **EXPERIMENTAL METHODS**

##### **Comparison to conventional containers**

A study was planned to measure changes in several properties through time for a coal sample stored in different container types. 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  $R_3$  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 mm coal in polyethylene buckets and foil laminate bags; -0.85 mm coal in steel cans, foil laminate bags and an open container exposed to the atmosphere. After 4, 16 and 52 weeks containers were opened and samples analyzed as had been done for the original sample.

##### **Comparison to Argonne Premium Coal Sample glass ampoules**

Argonne National Laboratory's Premium Coal Sample Program supplies coal samples in flame-sealed, nitrogen-filled glass ampoules (6). Six 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. Two of each were placed in a nitrogen-filled glovebox where they were opened and the contents resealed in foil

laminated bags. Two of each remained unopened. After eight months analyses comparing the coal resealed in foil laminate bags with that in the undisturbed ampoules were performed.

## RESULTS

### Thermoplastic Properties

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 ddpm with a fluid range of 100°C. Figure 4 shows that foil laminate bags maintain fluid range better than steel cans and much better than buckets. Maximum fluidity and free-swelling index showed similar trends.

For the Argonne premium samples, Table I shows that samples ANL-101 and -501 repackaged in foil laminate bags and stored for eight months compared well to those stored in their original ampoules. The variation in results for ANL-701 is probably caused by problems with the instrument, and for ANL-301, -401 and -601 the test could not be successfully completed on the amount of coal allocated because multiple repeat runs were required to meet the ASTM precision requirement (7).

### Sulfur Forms

Another sensitive indicator of deterioration, particularly in coals with abundant iron sulfide minerals, is the oxidation of sulfides to sulfates. Figure 5 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.

### Gaseous Oxygen

Oxygen levels in the containers' internal atmospheres were measured with a polarographic oxygen detector (Fig. 6). 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.

### Fluorescence

Alteration of vitrinite fluorescence intensity is measured with photometric readings taken at regular intervals during a period of constant irradiation with blue light. For freshly mined coal, alteration patterns change from positive in lignites to one showing a dual response (first decreasing then increasing) for high volatile coals and finally becoming negative in medium volatile coals. Recent work has shown that different mechanisms of photochemical oxidation may be responsible for the formation (positive alteration) and destruction (negative alteration) of fluorophoric sites during blue-light irradiation (8). When coal becomes weathered its pattern of alteration changes from dual to positive and the mean fluorescence intensity of vitrinite also decreases (9).

Fluorometric analysis of high volatile coals stored at -6 mm for more than 30 months shows that the positive component of alteration increases and mean fluorescence intensity ( $F_{1600}$ ) decreases with time. However, the alteration pattern for the medium volatile Lower Kittanning coal in this study is unchanged after 49 weeks of storage, whereas intensity decreases significantly (10). Thus, fluorescence intensity is a more sensitive measure of short-term storage changes in the medium volatile coal than alteration.

### Other Properties

The alkali extraction test for oxidation of bituminous coal was performed on all samples. According to this test, all containers of the Lower Kittanning sample allowed oxidation with a narrow range of results; -6 mm coal in foil bags was preserved best and the exposed sample fared worst. For the Argonne samples (Table 1), those repackaged in foil bags compared favorably to those in ampoules, but both readings tended to be lower than those on the original ampoules. The precision of this test has not yet been determined.

Total conversion and product yield were determined from tubing-bomb liquefaction experiments (350°C, 30 min, 1000 psig  $H_2$ , 2:1 tetralin to coal ratio) for samples stored for 4 and 16 weeks in foil laminate bags and 4 weeks in a polyethylene bucket. Although conversion ranged from 17.9 - 21.7% and oil yields from 2.5 - 3.3%, no significant difference attributable to storage methods was observed.

Selected samples were examined with FTIR; no significant differences in carbonyl ( $\sim 1600\text{ cm}^{-1}$ ) or aliphatic stretching ( $\sim 2920\text{ cm}^{-1}$ ) were found between the foil bag and bucket storage after 4 and 16 weeks.

## DISCUSSION

Conventional storage containers can cause sample deterioration. Based on this study and the desire to improve sample preservation in long-term storage, samples collected since December, 1989 for the Penn State Coal Sample Bank are being stored in foil laminate bags after processing. At this time all such samples are designated DECS (Department of Energy Coal Samples).

For field collection and temporary storage prior to processing, steel barrels with high-density gaskets (11) are employed. 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). This avoids the problem of poorer preservation of bulk samples caused by storage in a different container type.

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Table 1. Gieseler Fluidity and Alkali Extraction Data for Argonne Premium Coal Samples

	ANL-101, Upper Freeport, mvb			ANL-301, Illinois #6, hvBb		
<u>Gieseler Fluidity</u>	As Rec'd	Stored in Ampoule	Stored in foil bag	As Rec'd	Stored in Ampoule	Stored in foil bag
max. fluidity, ddpm	29,998	29,934	29,910	72	54	
initial fluidity T, °C	381	376	386	368	367	test
max. fluidity T, °C	456	456	454	418	413	failed
solidification T, °C	507	502	498	447	444	
fluid range, °C	126	126	112	79	77	
<u>Alkali Extraction</u>						
% transmittance	94.5	91.7	87.7	95.3	86.2	91.1
	ANL-401, Pittsburgh, hvAb			ANL-501, Pocahontas #3, lvb		
<u>Gieseler Fluidity</u>	As Rec'd	Stored in Ampoule	Stored in foil bag	As Rec'd	Stored in Ampoule	Stored in foil bag
max. fluidity, ddpm	25,055	17,093		46	39	37
initial fluidity T, °C	386	384	test	453	444	445
max. fluidity T, °C	438	430	failed	486	480	484
solidification T, °C	475	473		515	511	508
fluid range, °C	89	89		62	67	63
<u>Alkali Extraction</u>						
% transmittance	96.4	91.8	91.5	97.9	95.4	95.1
	ANL-601, Blind Canyon, hvBb			ANL-701, Lewiston-Stockton, hvAb		
<u>Gieseler Fluidity</u>	As Rec'd	Stored in Ampoule	Stored in foil bag	As Rec'd	Stored in Ampoule	Stored in foil bag
max. fluidity, ddpm	2	2		112	12	119
initial fluidity T, °C	404	398	test	410	406	409
max. fluidity T, °C	424	415	failed	445	422	437
solidification T, °C	446	438		469	431	463
fluid range, °C	41	40		59	25	54
<u>Alkali Extraction</u>						
% transmittance	96.0	89.9	87.6	95.7	81.7	90.9

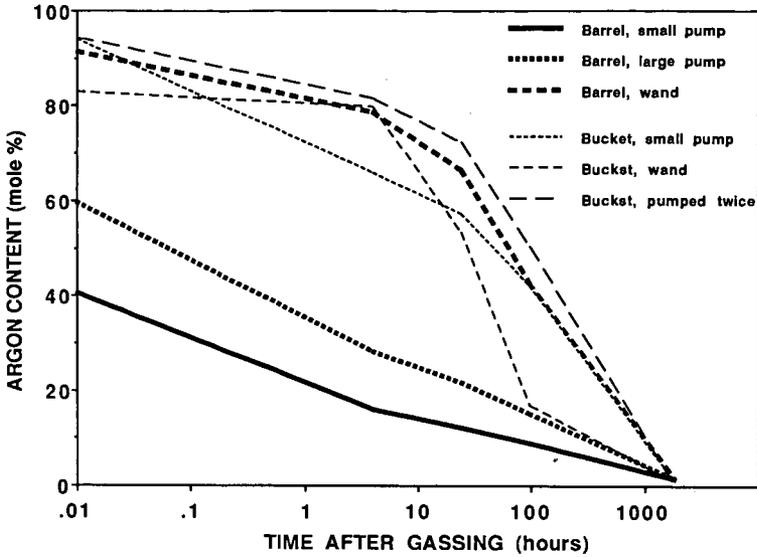


Figure 1. Argon in Barrel and Bucket Atmospheres

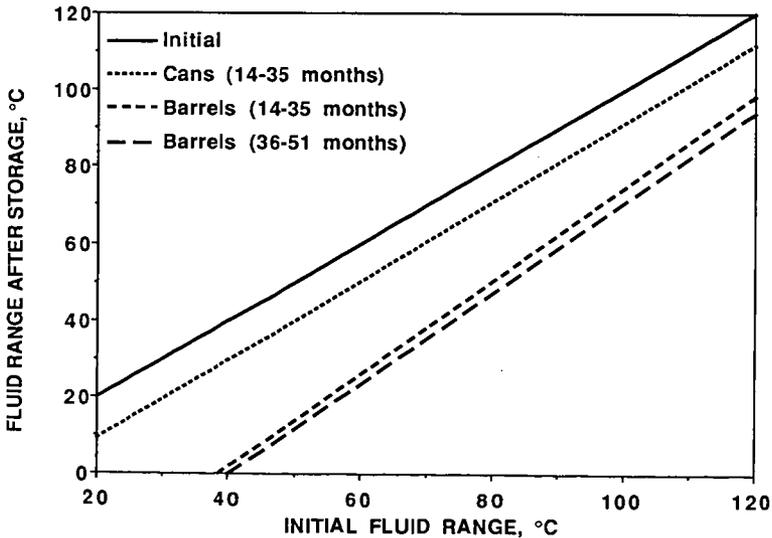


Figure 2. Gieseler Fluid Range: Linear Regression on 28 Samples

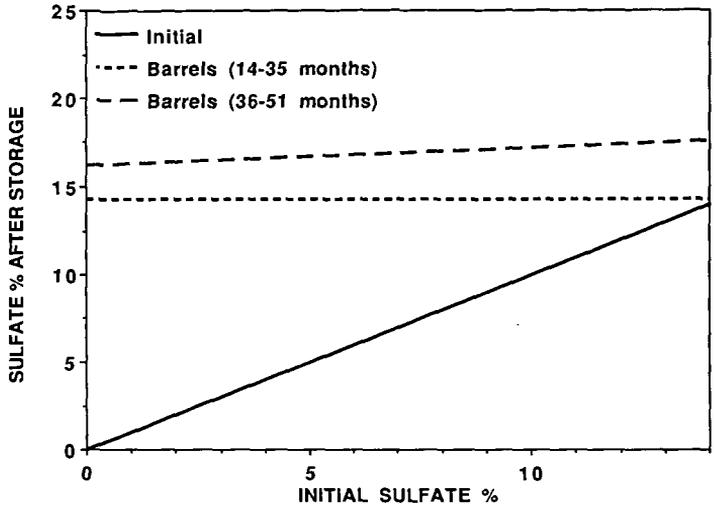


Figure 3. Sulfate Sulfur as % of Total Sulfur: Linear Regression on 53 samples

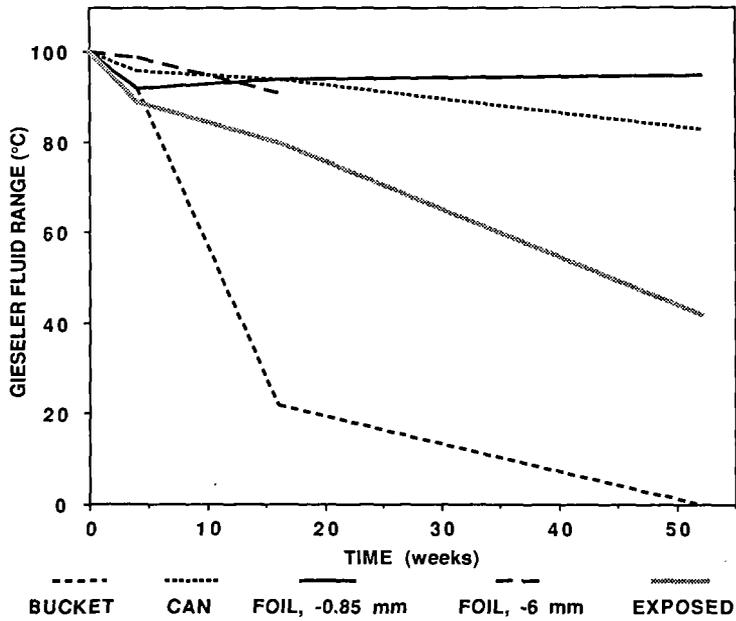


Figure 4. Gieseler Fluid Range of mvb Lower Kittanning Seam Sample

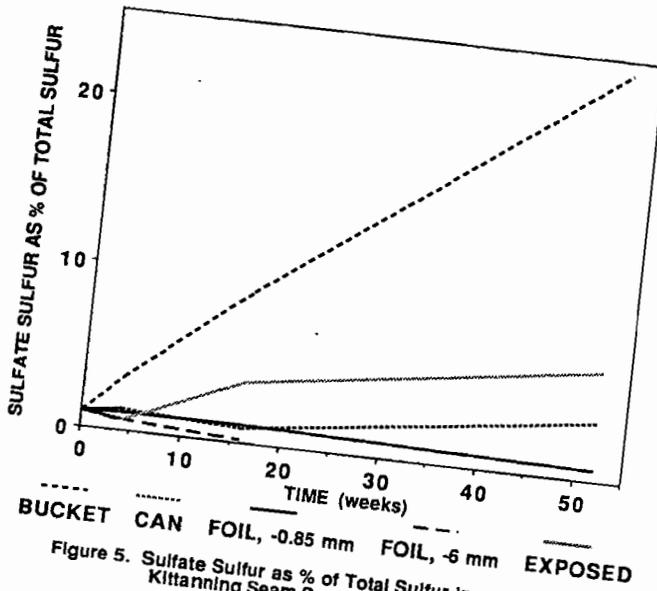


Figure 5. Sulfate Sulfur as % of Total Sulfur in mvb Lower Kittanning Seam Sample

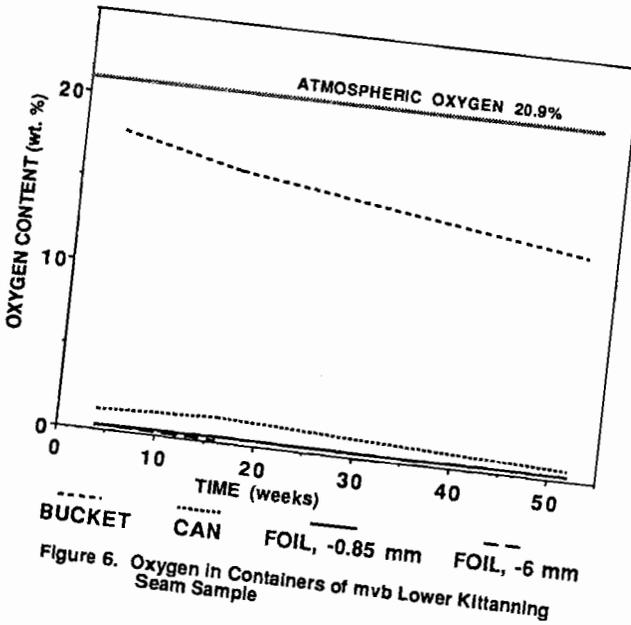


Figure 6. Oxygen in Containers of mvb Lower Kittanning Seam Sample