Preliminary evaluation of Halocarbon 0.8 oil's impact on metallurgical coal quality

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Abstract. Heavy organic liquids are typically used for coal laboratory float and sink testing. Perchloroethylene (PCE), methylene bromide and naphtha are typical liquids used in labs worldwide to create baths with a wide range of specific gravities. All three of these liquids are harmful to human health and can have negative effects on coal rheology. Perchloroethylene is a solvent that has been used to remove organic sulfur from coal prior to use in power generation plants. The PCE acts as a swelling agent and when heated in the presence of a catalyst, will cleave the C-S bonds, removing organic sulfur from the coal. PCE is a clear liquid however after the float and sink process it turns shades of yellow to dark brown. Portions of the coal become suspended in solution and many organically bound elements are released from the coal into the solution. This may result in certain elements being underestimated in the clean coal products arising from perchloroethylene based float and sink. The float and sink test assesses metallurgical coal washability using organic liquids, but traditional options like naphtha, perchloroethylene, and methylene bromide pose health risks. This study examines the effects of four liquids on coal quality and chemistry.

1 Introduction:

In the metallurgical coal industry, most exploration coal drill core samples are subjected to the float and sink test in coal testing laboratories to determine the coal's washability characteristics [1]. During this procedure a representative coal sample is sized, removing the minus 0.50mm (in the case of this study) or minus 0.25mm material which usually will be treated by froth flotation in case of metallurgical coals. The plus 0.50 mm coal is placed in a series of liquids with known increasing specific gravities (s.g) in equal s.g. intervals (1.3, 1.4, 1.5 etc.). Particles that float on the surface of the liquid are called a "float" fraction, and these have a lower density than the liquid. Particles that sink are called "sink" fractions and have a higher density than the liquid [2]. Each float fraction is analysed at a minimum for ash and often analysed for proximate analysis, free swelling index and sulfur. The float and sink data determine the coal's washability and its beneficiation potential [1]. Also, washability data provides crucial information for the design of coal preparation plants [2].

Traditionally organic liquids such as naphtha (specific gravity 0.75), perchloroethylene (specific gravity of 1.62) and methylene bromide (specific gravity of 2.47) are used to create baths with densities varying from 1.30 to 2.20 SG. These liquids are inexpensive and provide baths with stable specific gravities however these liquids are harmful to human health.

Naphtha solvent with the molecular formula of CnH2n, where n is between 5 and 8. Naphtha is a complex mixture of hydrocarbons that is a petroleum distillate which is a colorless and highly flammable liquid with a specific gravity of 0.659. It can cause skin irritation and may lead to dizziness or drowsiness when inhaled. Prolonged or repeated exposure can result in organ damage, and if swallowed, it poses a fatal risk by entering the airways [3].

Perchloroethylene, also known as tetrachloroethylene, is a colorless, non-flammable liquid with the chemical formula C_2Cl_4 and a specific gravity of 1.62. It has historically been used as a cleaning solvent in the dry-cleaning industry. Inhalation of its fumes can irritate the eyes and upper respiratory tract, and prolonged exposure can lead to neurological effects, as well as kidney and liver damage. It is classified as a probable carcinogen, and therefore poses significant health risks to laboratory operators and must be handled with caution to ensure safety [4] [5] [6]. A patent exists that describes a method for using perchloroethylene as a solvent to remove organically bound sulfur from coal. In this process, the coal is added to perchloroethylene with a catalyst which breaks carbon-sulfur bonds, liberating sulfur from the coal [7].

Methylene bromide (CH_2Br_2), also known as dibromomethane, is a colorless liquid with a sweet odor, primarily used as a solvent and to make other chemicals. It is highly hazardous, posing risks to both human health and the environment. Inhalation can cause dizziness, drowsiness, and respiratory irritation, and it can absorb through the skin with prolonged exposure resulting in liver and kidney damage [8].

Alternative liquids have been investigated for their usefulness in the float and sink method. Mackay et al., 2023 studied Novec 7200 and FC-770 fluids designed and manufactured by 3M. These were liquids traditionally used in vapor degreasing and heat transfer fluid for electronics. The liquids worked well and were not harmful to human health however they were very costly, and they stopped being produced [9].

The fluid produced by the company Halocarbon was found to be a good candidate for study. Halocarbon fluid is also known as polychlorotrifluoroethylene (CF_2CClF) n and has traditionally been used as a lubricating oil. The liquid is not classified as dangerous for supply/use. It is non-toxic, nonhazardous, chemically inert and a boiling point greater than 133 degrees Celsius [10].

At least one metallurgical coal mine in Canada has been using Halocarbon 0.8 for their float and sink process since the late 1990s. They have had no safety issues and there were no noticeable effects on coal quality.

2 Objectives

The purpose of this study was to determine the effects that soaking coal in different organic liquids had on its quality:

1. Effects of soaking in organic liquids on coal quality
2. Effects of soaking in organic liquids on coal chemistry

Four liquids were evaluated: naphtha, perchloroethylene, methylene bromide, and Halocarbon 0.8.

3 Methodology

A clean metallurgical coal sample was collected from an industrial coal processing plant and sent to Birtley Coal & Minerals Testing Laboratory in Calgary. The coal sample was screened at -0.50 mm and six subsamples were removed from + 0.50 mm size fraction in the clean sample and one was kept as the "control sub sample". The + 0.50 mm size fraction was used for studying the organic liquids typically used in laboratory float and sink analysis because the - 0.50 mm size fraction undergoes froth flotation and is not typically subjected to washability study using these liquids.

3.1 Soak tests

For each liquid type, one glass jar was filled with 1000 ml of the liquid. A photo was taken of the liquid. A coal sample with a mass of 495 grams was added to each liquid and stirred. The coal and liquid were allowed to sit for five minutes. A photo of the coal/liquid blend was taken. The coal was then removed and laid to air dry. A photo of the remaining liquid was taken and color changes noted. Liquid was saved for later testing.

3.2 Coal quality

After soaking the coal samples and air drying, the samples were tested at Birtley Coal & Minerals Testing for the following coal quality parameters:

1. Proximate analysis ASTM
2. Total Sulfur ASTM
3. Free swelling index ASTM
4. Hardgrove grindability index
5. Gieseler fluidity ASTM
6. Ruhr Dilatation ASTM

3.3 Trace metals analysis of filtered liquid samples

The liquids were retained after the soaking test and sent to Intertek Chemicals and Pharmaceuticals in Allentown Pennsylvania for trace elements analysis. The intent with this test was to determine if chemically bound elements were released from the coal during the soaking test. The trace element concentrations were analysed using sector field inductively coupled plasma mass spectrometry (SFICP-MS) and inductively coupled plasma optical emission spectroscopy (ICP-OES).

Samples were digested using a Milestone Ultrawave 3 Single Reactor Chamber instrument with a microwave-assisted method involving nitric and hydrochloric acids. Each preparation included a spiked sample, a dilution control with known element concentrations, and a blank to ensure accuracy. A minimum of two isotopes or analysis modes were employed in the analytical sequence to confirm concentrations and evaluate spectra for potential interferences.

ICP-MS analysis was carried out using a Thermo Scientific Element 2 ICP-MS, with twelve-point linear calibration curves ranging from 0.05 ppbw to 100 ppbw. Calibration standards were prepared from certified traceable multi-element stock solutions. Whenever possible, at least two isotopes or resolutions were utilized to verify concentrations and examine spectra for potential interferences. A 10ppb quality control check was conducted during sample analysis.

ICP-OES analysis was performed on the samples using a Perkin Elmer Optima 5300 optical emission spectrometer. Each sample analyzed underwent duplicate determination. Calibration standards, prepared from multi-element stock solutions, ranged in concentration from 0.01 ppm to 5 ppm. At least two wavelengths were used in the analysis sequence to confirm concentrations and assess spectra for potential interferences. Sample analysis was bracketed by calibration blank and standard solution measurements, with a 1 ppm quality control check conducted during the process.

The liquids were analysed for the concentration of 119 elements listed in Table 1.

Table 1. Elements analysed in organic liquids.

Silver, Ag	Holmium, Ho	Ruthenium, Ru
Aluminum, Al	Indium, In	Sulfur, S
Arsenic, As	Iridium, Ir	Antimony, Sb
Gold, Au	Potassium, K	Scandium, Sc
Boron, B	Lanthanum, La	Selenium, Se
Barium, Ba	Lithium, Li	Silicon, Si
Beryllium, Be	Lutetium, Lu	Samarium, Sm
Bismuth, Bi	Magnesium, Mg	Tin, Sn
Calcium, Ca	Manganese, Mn	Strontium, Sr
Cadmium, Cd	Molybdenum, Mo	Tantalum, Ta
Cerium, Ce	Sodium, Na	Terbium, Tb
Cobalt, Co	Niobium, Nb	Tellurium, Te
Chromium, Cr	Neodymium, Nd	Thorium, Th
Cesium, Cs	Nickel, Ni	Titanium, Ti
Copper, Cu	Osmium, Os	Thallium, Tl
Dysprosium, Dy	Phosphorous, P	Thulium, Tm
Erbium, Er	Lead, Pb	Uranium, U
Europium, Eu	Palladium, Pd	Vanadium, V
Iron, Fe	Praseodymium, Pr	Tungsten, W
Gallium, Ga	Promethium, Pm	Yttrium, Y
Gadolinium, Gd	Platinum, Pt	Ytterbium, Yb
Germanium, Ge	Rubidium, Rb	Zinc, Zn
Hafnium, Hf	Rhenium, Re	Zirconium, Zr
Mercury, Hg	Rhodium, Rh	

4 Results

Photos of the liquid, liquid+coal and filtered liquid after removal of the coal were taken. Some liquids remained clear before and after the soak test. Others changed to a darker color implying a chemical reaction between the liquid and coal.

4.1 Soak tests

4.1.1 Naphtha

Fig. 1. Naphtha soaking test photos.

Figure 1 shows the steps in the coal soaking process. The naphtha was clear and colorless prior to the soaking test and after the removal of the coal. Visually, it did not appear to have reacted (physically or chemically) with the coal sample.

4.1.2 Perchloroethylene

Fig. 2. Perchloroethylene soaking test photos

Figure 2 shows the photos taken before, during and after the coal soaking test in perchloroethylene. The perchloroethylene was clear and colorless prior to the soaking test and then changed to a light brown color after the coal was removed. This implied that the liquid reacted either physically or chemically with the coal, with some chemical elements from the coal remaining in solution.

4.1.3 Methylene bromide

Fig. 3. Methylene bromide soaking test photos.

Figure 3 shows the photos of the soaking test for methylene bromide. The Methylene bromide was clear and colorless prior to the soaking test and dark brown to black after removing the coal. Methylene bromide changed color the most post soaking implying a physical and or chemical interaction between the liquid and coal.

4.1.4 Halocarbon 0.8

Fig. 4. Halocarbon 0.8 soaking test photos

Figure 4 shows the before, during and after photos of the soak test in Halocarbon 0.8. Halocarbon 0.8 liquid was colorless and clear prior to soaking and remained the same after the removal of the coal, implying no reaction with the coal.

In addition to noting color changes with the liquid, the specific gravity of the liquids was measured before and after the soaking test. The mass of the coal was also measured before and after the soaking tests. Table 2 shows the results.

Table 2. Coal soak test observations

Bath	Sample wt before (g)	Sample wt after (g)	SG before	SG after	Liquid colour before	Liquid colour after
naphtha (SG ~0.75)	495	496	0.729	0.729	clear	clear
perchloroethylene (SG ~1.62)	495	493	1.614	1.614	clear	orange
methylene bromide (SG ~2.47)	495	501	2.460	2.460	yellow tint	dark brown
Halocarbon 0.8 oil (SG ~1.70)	495	493	1.748	1.746	clear	clear
Control (no soaking)	495	495	-	-	-	-

The specific gravity of the liquids remained relatively constant before and after the soaking test. The mass of the coal samples remained mostly constant except for the coal soaked in methylene bromide. The methylene bromide seemed to have absorbed onto/into the coal enough to increase the mass of the coal sample by 5 grams.

4.2 Coal quality

Table 3 summarizes the proximate analysis, chlorine, fluorine, free swelling index (FSI) and hardgrove grindability index (HGI). Each set of analyses can be compared to the control sample to determine how each liquid affected the coal quality. All ash values reported to within 0.36% on an air-dried basis when compared to the control. It should be noted that the sample soaked in methylene bromide reported over double the air-dried moisture when compared to the control. The methylene bromide did not readily evaporate from the soaked coal sample. This also added to the increase in the mass of the coal sample as discussed in section 4.1. The volatile matter and fixed carbon values did not vary by much for all samples when compared to the controls sample. With respect to FSI, methylene bromide resulted in a decrease of 0.5 when compared to the control sample. All other values remained the same. The HGI was in the same range or within 4 points of the control sample. Since perchloroethylene, methylene bromide and halocarbon all contain chlorine it's not surprising that the soak samples all had higher chlorine values than the control sample. Samples were rinsed with acetone and tested again, which lowered the chlorine content but did not bring it back down to the control value. The control sample was also rinsed and resulted in lowering the chlorine content of that sample as well. This means that the acetone strips organically bound chlorine from coal. Methylene bromide and both halocarbon liquids contain fluorine. Rinsing with acetone was successful in removing the fluorine to comparable levels to the control sample.

Table 3. Coal quality after soak testing

Coal Analysis, air dried basis												
Sample ID	MOIST%	ASH%	VOL%	F.C.%	S%	Chlorine ppm as is	Chlorine ppm rinsed	Fluorine ppm as is	Fluorine ppm rinsed	FSI	H.G.I.	BASIS
+0.5mm	0.88	9.32	23.12	66.68	0.43	206	89	188	192	7.0	77	adb
Naphtha		9.40	23.33	67.27	0.43	208	90	190	194			db
+0.5mm	0.88	9.34	23.16	66.62	0.44	1675	340	202	217	7.0	75	adb
Perchloroethylene		9.42	23.37	67.21	0.44	1690	343	204	219			db
+0.5mm	1.94	9.75	22.66	65.65	0.42	8288	4604	724	207	6.5	76	adb
Methylene Bromide		9.94	23.11	66.95	0.43	8452	4695	738	211			db
+0.5mm	0.92	8.98	23.27	66.83	0.44	740	99	1049	218	7.0	77	adb
Halocarbon 0.8 Oil		9.06	23.49	67.45	0.44	747	100	1059	220			db
+0.5mm	0.68	8.94	23.45	66.93	0.44	208	70	221	197	7.0	77	adb
Control		9.00	23.61	67.39	0.44	209	70	223	198			db

The rheological properties of coal were tested on all samples. Giesler fluidity temperatures and maximum fluidity were measured for all samples (Table 4). All temperatures were similar to the control as well as the temperature range. Maximum fluidity values were already quite low with the control being 10.1 ddpm. The perchloroethylene and methylene bromide resulted in lower fluidity values than the control and the Naphtha and Halocarbon 0.8 oil resulted in slightly higher max fluidity numbers. All samples were run on the same date so that ageing wouldn't factor in lowering the fluidity numbers.

Table 4. Gieseler fluidity after soak test

LIQUID	TEMPERATURES °C					
	INITIAL SOFT TEMP (1 DDPM)	MAX. FLUIDITY TEMP	SOLIDIFI-CATION TEMP	TEMP RANGE	MAX. FLUIDITY DDPM	RUN DATE
Naphtha	436	466	497	61	**12.1**	23-Aug
Perchloroethylene	438	461	491	53	**6.6**	23-Aug
Methylene Bromide	431	453	484	53	**4.8**	23-Aug
Halocarbon 0.8 Oil	438	464	494	56	**13.4**	23-Aug
Control	437	465	497	60	**10.1**	23-Aug

Table 5 summarizes the Ruhr dilatation test results. All samples were run on the same date to remove ageing as a variable in the dilatation numbers. The softening temperatures were very similar for all samples. The temperature at maxmum contraction was considerably lower for the methylene bromide sample, where it was 24 points lower than the control sample. The maximum contraction was very similar for all other samples.

Table 5. Ruhr dilatation after soak test

LIQUID	SOFTENING TEMPERATURE	TEMPERATURE MAX CONTRACTION	TEMPERATURE MAX DILATATION	% CONTRACTION	% DILATATION	TOTAL % DILATATION	%SD2.5	RUN DATE
Naphtha	403	484	-	20	-	-	-	22-Aug
Perchloroethylene	403	472	-	22	-	-	-	22-Aug
Methylene Bromide	400	460	-	23	-	-	-	22-Aug
Halocarbon 0.8 Oil	403	481	-	20	-	-	-	22-Aug
Control	403	484	-	20	-	-	-	22-Aug

4.3 Trace metals analysis of filtered liquid samples

The concentration of 119 elements were measured in both unused liquid naphtha, perchloroethylene, methylene bromide, and halocarbon 0.8, and the liquids after soaking with coal. Most elements were not present in the liquids either before or after soaking.

Table 6 summarizes the concentration of several elements found in the naphtha after soaking with coal. Boron, calcium, copper, iron, molybdenum, selenium, strontium and zinc were found to have leaching into solution from the coal.

Table 6. Element concentration in used naphtha.

Element	Unused Naphtha (ppm)	Used Naphtha (ppm)
Boron, B	<0.002	0.011
Calcium, Ca	<0.029	0.12
Copper, Cu	<0.029	0.045
Iron, Fe	<0.019	0.039
Molybdenum, Mo	<0.001	0.32
Selenium, Se	<0.015	0.072
Strontium, Sr	<0.001	0.002
Zinc, Zn	<0.005	0.022

Table 7 summarizes the concentration of two elements found in the perchloroethylene after soaking with coal. Calcium and selenium were found to have leached into solution during the soaking of the coal.

Table 7. Element concentration in used perchloroethylene.

Element	Unused Perchloroethylene (ppm)	Used Perchloroethylene (ppm)
Calcium, Ca	<0.034	0.20
Selenium, Se	<0.053	0.13

Table 8 summarizes the concentration of silver, aluminum, beryllium, calcium, cobalt, gallium, magnesium, sodium, niobium, osmium, platinum, rhodium, sulfur and selenium that leached from the coal into methylene bromide after soaking.

Table 8. Element composition in used methylene bromide.

Element	Unused Methylene Bromide (ppm)	Used Methylene Bromide (ppm)
Silver, Ag	≤0.002	0.003
Aluminum, Al	<0.063	0.17
Beryllium, Be	<0.001	0.004
Calcium, Ca	<0.025	2.5
Cobalt, Co	<0.002	0.004
Gallium, Ga	≤0.004	0.005
Magnesium, Mg	≤0.10	0.12
Sodium, Na	<0.019	0.14
Niobium, Nb	0.67	1.6
Osmium, Os	<0.003	0.092
Platinum, Pt	≤0.003	0.005
Rhodium, Rh	<0.001	0.003
Sulfur, S	0.30	1.8
Selenium, Se	<0.013	0.068

No elements leached into the Halocarbon 0.8 oil from the soaking of coal. This result suggests that Halocarbon 0.8 oil is perhaps the most inert liquid analysed in this study.

The only liquid that did not seem to leach trace elements from the coal was Halocarbon 0.8. Perchloroethylene only leached calcium and selenium from the coal. Naphtha, and methylene bromide leached several trace elements from the coal samples. The liquid that leached the most trace elements was methylene bromide.

5 Conclusion

This study evaluated the effects of soaking metallurgical coal in different organic liquids commonly used in float and sink testing while comparing those results to an alternative liquid called Halocarbon 0.8.

Coal quality testing showed that proximate analysis, FSI, and HGI remained relatively constant across most samples, except for coal that was soaked in methylene bromide - which resulted in an increase in air-dried moisture and a decrease in FSI. The chlorine and fluorine content in the perchloroethylene, methylene bromide, and halocarbon-soaked samples were higher than the control, however acetone rinsing reduced, but did not eliminate the elevated values.

Trace metals analysis indicated that methylene bromide leached the highest number of elements from the coal, including silver, aluminum, and selenium. Naphtha also leached several elements, while perchloroethylene leached calcium and selenium. Halocarbon 0.8 was the most inert, with no measurable leaching of elements.

From a safety perspective, the use of methylene bromide, perchloroethylene, and naphtha presents significant health hazards, including respiratory irritation, neurological effects, and potential carcinogenicity. Methylene bromide, in particular, poses risks of acute toxicity, and prolonged exposure can cause organ damage. Proper handling, including the use of personal protective equipment (PPE), adequate ventilation, and careful disposal, is necessary to mitigate these risks. In contrast, Halocarbon 0.8 is a safer alternative, with no hazard classification, making it a preferable choice for laboratory and industrial applications where worker safety is a priority.

These findings suggest that Halocarbon 0.8 is a viable alternative to traditional organic float and sink liquids due to its chemical inertness, lack of health risks and lack of adverse effects on coal properties.

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