Dust Suppressant and Process Additive Impacts on HCC Coke Properties

November 2020

Outline:

Safety Share – GHS

Process Additives - Overview

Characterization of Additives

Key Concerns for Coke Quality

Case Study 1 – Antifreeze/Side Car Release

Case Study 2 – Car Topper Dust Suppressant

Case Study 3 – Conveyed Dust Suppression Additive

Case Study 4 – Flowability Aid

Summary

Safety Share

Global Harmonized System (GHS) for Chemical Safety Data Sheets

- GHS adopted by UN in 2003
- Adopted in Canada in 2015, finalized 2018.
- Goal for consistent rules around the world.
- Some products appear to change hazards / risks but really just standardization.
- Removes ambiguity and biases, provides better clarity and consistency.

- Categories: Health **Hazards**, Physical **Hazards** and Environmental **Hazards**.
- Classes: 29 different, 17 Health, 10 Physical, 2 Environmental.
- Hazard Categories: 1 (most severe) to 4 (least severe).

Common Process Additives for Coal Operations

Road Dust Suppression

Flowability Aid

Railcar Car Topper
Side Car Release

Stockpile Dust
Suppressant

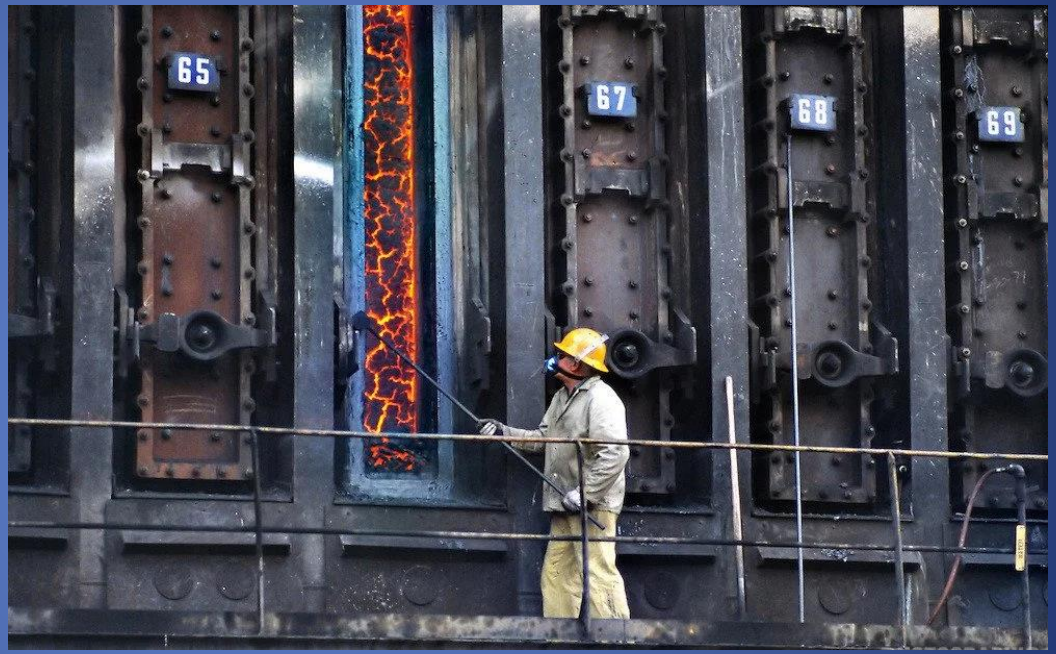
Truck Side Release

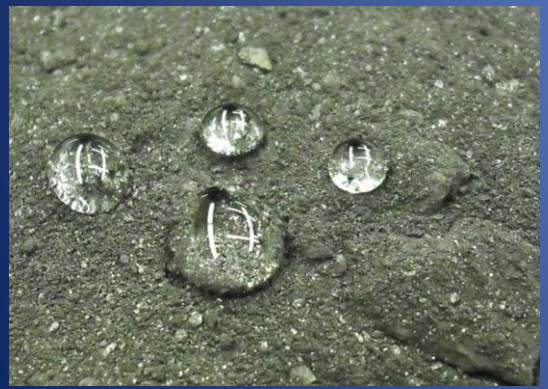
Conveyed Fugitive Dust Suppression

Why the concern?

Notable Qualities of Western Canadian Coal:

- Unique Mid-Vol products,
- High inert levels,
- High coke strength,
- Lower wall and gas pressure,
- Favourable ash chemistry.
- Concerns are primarily impurities and alkali earth metals (Na, K) that will affect rheology/petrography.
- Practical concerns include not affecting bulk density, critical micro-elements.





Potential Chemical Additive Concerns

Additive	Key Concern	Quality Impact
Surfactants (conveyed dust suppressants)	Coal surface character	Bulk density, Fluidity, Dilatation.
Polymers (car topper, stockpile dust suppressants)	Coal surface character & Alkali Earth metals	Bulk density, Fluidity, Dilatation
Polymers (car topper, stockpile dust suppressants)	Volatility during coking process	Coke oven pressure
Flowability additives	Coal surface character, impurities	Bulk density, Fluidity, Dilatation, Petrography
Antifreeze (side car release, belt & truck antifreeze)	Impurities Coal surface character	Fluidity, Dilatation

Case Study 1. Side Car Release

Key concerns: impurities, coal quality impact.

- Known impurity problems: Sodium, Potassium, Calcium, Magnesium, Silicon, Chlorides.
- Disqualifies: Salt-based antifreezes.
- Product C has total of <4800 ppm.
- **As applied at 100 ppm, total is 0.48 ppm.**

ELEMENTS BY ATOMIC SPECTROSCOPY (LIQUID)				
ID		DD3265	DD3266	DD3267
Sampling Date		2012-04-10	2012-04-10	2012-04-10
	Units	**Product A**	**Product B**	**Product C**
Total Metals by ICP				
Total Aluminum (Al)	mg/kg	1.7	0.5	1.3
Total Antimony (Sb)	mg/kg	0.5	<0.5	<0.5
Total Arsenic (As)	mg/kg	<0.3	<0.3	<0.3
Total Barium (Ba)	mg/kg	0.03	0.05	<0.01
Total Beryllium (Be)	mg/kg	<0.03	<0.03	<0.03
Total Bismuth (Bi)	mg/kg	<0.5	<0.5	<0.5
Total Boron (B)	mg/kg	<0.1	618	0.9 (1)
Total Cadmium (Cd)	mg/kg	<0.05	<0.05	<0.05
Total Chromium (Cr)	mg/kg	<0.1	<0.1	<0.1
Total Cobalt (Co)	mg/kg	<0.2	<0.2	<0.2
Total Copper (Cu)	mg/kg	<0.2	<0.2	<0.2
Total Iron (Fe)	mg/kg	26.1	1.4	26.8
Total Lead (Pb)	mg/kg	<0.3	<0.3	<0.3
Total Lithium (Li)	mg/kg	<0.2	<0.2	<0.2
Total Manganese (Mn)	mg/kg	0.11	<0.03	0.09
Total Molybdenum (Mo)	mg/kg	<0.2	<0.2	<0.2
Total Nickel (Ni)	mg/kg	<0.2	<0.2	<0.2
Total Phosphorus (P)	mg/kg	344	11.1	355
Total Selenium (Se)	mg/kg	<1	<1	<1
Total Silicon (Si)	mg/kg	9.0	11.2	5.9
Total Silver (Ag)	mg/kg	<0.1	<0.1	<0.1
Total Strontium (Sr)	mg/kg	0.12	0.15	0.02
Total Tin (Sn)	mg/kg	<0.3	<0.3	<0.3
Total Titanium (Ti)	mg/kg	<0.05	0.35	<0.05
Total Vanadium (V)	mg/kg	<0.1	<0.1	<0.1
Total Zinc (Zn)	mg/kg	0.46	0.24	0.43
Total Zirconium (Zr)	mg/kg	0.4	0.3	0.3
Total Calcium (Ca)	mg/kg	22.1	30.9	3.3
Total Magnesium (Mg)	mg/kg	19.8	10.0	14.1
Total Potassium (K)	mg/kg	165	13	159
Total Sodium (Na)	mg/kg	4440	1770	4560
Total Sulphur (S)	mg/kg	5980	341	6160
Total Fe, Ca, Mg, K, Na)		4673	1825.3	4763.2

Case Study 1. Side Car Release

- Direct Coal Testing:
- Na, K show no significant difference,
- Total Alkali in ash identical

Coal Quality Testing		Original Results		Repeat Results	
		Standard Control	Standard Treated	Standard Treated	Standard Treated
			Porduct A	Product B	Product C
Ash Analysis - % of Ash (db)					
SiO2	%	54.45	54.80	56.40	55.10
Al2O3	%	31.20	31.33	31.30	31.40
TiO2	%	1.63	1.67	1.62	1.70
CaO	%	1.79	1.80	1.68	1.79
K2O	%	0.67	0.67	0.69	0.64
Na2O	%	0.04	0.05	0.03	0.05
MgO	%	0.76	0.86	0.58	0.65
Fe2O3	%	6.16	6.75	5.69	6.47
P2O5	%	1.02	0.94	0.94	0.98
SO3	%	0.60	0.72	0.65	0.72
Chemistry of Ash or Coal (db)					
Alk (Fe,Ca,Mg,K,Na) in Ash	%	9.42	10.13	8.67	9.60
Alk Ash in Coal (db)(Na,K)	%	0.05	0.05	0.05	0.05
Ash Basicity Index (Fe+Ca+Mg+K+Na)/(Si+Al)		0.11	0.12	0.10	0.11
P in Coal (db)	%	0.043	0.039	0.040	0.041

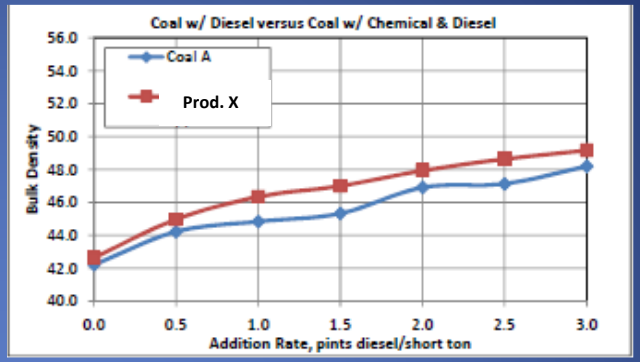
Case Study 1. Side Car Release

- Direct Coal Testing:
- Calorific value
- Thermal Rheology
- Petrography

- Confirmed no significant impact on coal quality.

			Standard Control	Standard Treated Prod A		Standard Treated Prod B	Standard Treated Prod C		Prem Treated Prod A	Prem Control		Prem Treated Prod B	Prem Treated Prod C
Calorific Value													
	GAD	kcal/kg	7698	7759		7758	7745		7716	7707		7726	7715
	NAR	kcal/kg	6718	6785		6790	6784		6881	6842		6874	6866
THERMAL RHEOLOGY													
FSI		-	9	9		7.5	8.5		9	8		9	7.5
Gieseler	start temp	deg C	424	420		418	421		417	418		414	415
	resolidification	deg C	493	490		490	491		487	486		486	487
	range	deg C	69	70		72	70		70	68		72	72
MF	Max Fluidity (MF)	ddpm	138	130		156	144		175	164		166	186
	log MF	-	2.14	2.11		2.19	2.16		2.24	2.21		2.22	2.27
Dilatation	softening temp	deg C	402	404		401	400		398	390		394	396
	max dil temp	deg C	471	471		467	468		466	464		462	464
	range	deg C	69	67		66	68		68	74		68	68
Dilatation	contraction	%	16	17		20	18		18	15		16	17
	dilatation, sd 2.5	%	14	14		18	16		14	19		18	17
	c+d	%	30	31		38	34		32	34		34	34
	log (c+d)	-	1.48	1.49		1.58	1.53		1.51	1.53		1.53	1.53
Sole Heat Oven - exp/contr(-)		%											
PETROGRAPHY - (Volume %, Mean Maximum Reflectance)													
V-types	8		0.0	0.0		0.0	0.0		0.0	0.0		0.0	0.0
	9		0.7	1.0		0.8	0.8		2.4	1.1		0.3	1.7
	10		2.9	5.0		6.4	6.7		16.6	12.1		17.0	13.3
	11		5.4	6.6		10.8	9.2		30.2	33.6		31.1	29.7
	12		19.4	19.1		20.6	21.2		4.3	7.0		5.7	11.6
	13		19.9	17.8		12.4	17.3		0.0	0.0		0.0	0.3
	14		0.7	2.9		0.5	0.6		0.0	0.0		0.0	0.0
	15		0.0	0.0		0.0	0.0		0.0	0.0		0.0	0.0
	16		0.0	0.0		0.0	0.0		0.0	0.0		0.0	0.0
	17		0.0	0.0		0.0	0.0		0.0	0.0		0.0	0.0
Vitrinite		%	**49.1**	**52.4**		**51.5**	**55.7**		**53.4**	**53.8**		**54.1**	**56.5**
Exinite		%	0.6	0.4		0.4	0.5		1.5	1.5		2.4	1.1
Reactive Semifusinite		%	15.9	15.6		15.8	13.7		13.7	13.5		13.1	12.7
Total Reactives		%	**65.6**	**68.4**		**67.7**	**69.9**		**68.6**	**68.8**		**69.6**	**70.3**
Inert Semifusinite		%	15.9	15.8		15.8	13.7		13.7	13.5		13.2	12.7
Micrinite/Macrinite		%	8.8	0.5		0.7	0.5		2.5	2.5		2.5	2.8
Fusinite/Inertodetrinite		%	3.5	8.2		8.3	8.3		10.3	10.2		9.1	8.7
Mineral Matter		%	5.3	5.3		5.3	5.3		4.9	5.0		5.0	5.3
Total Inerts		%	**34.4**	**31.6**		**32.3**	**30.1**		**31.4**	**31.2**		**30.4**	**29.7**

Case Study 2. Car Topper Dust Suppressant – 1st Generation



Key concerns: impurities, bulk density impact.

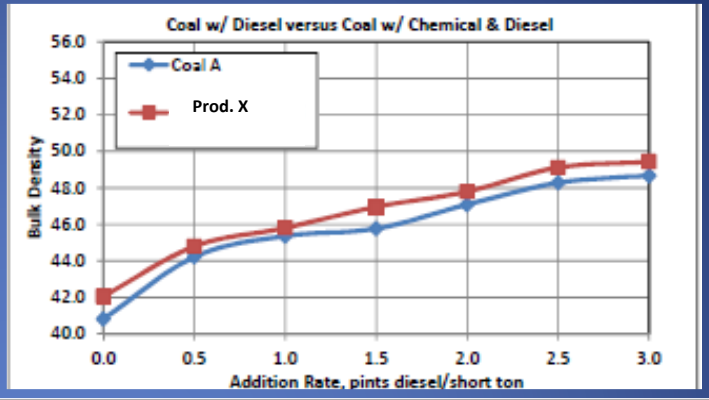
- Improved BD,
- Slight lower shift in Fluidities, larger plastic range.
- ARNU Dilatation almost identical,
- Max and Total Dilatation slightly higher.
- Overall within acceptable limits.

			Coal A	Coal A with Prod. X
GIESELER PLASTOMETER				
Maximum Fluidity	ASTM D2639	D.D.P.M.	376	371
Temperature at Maximum Fluidity		°C	458	451
Initial Softening Temperature (DDPM)		°C	420	412
Final Fluid Temperature		°C	483	480
Plastic Range		°C	66	71
Solidification Temperature		°C	486	483
AUDIBERT - ARNU DILATOMETER				
Maximum Contraction	ASTM D5515-97	%	25	25
Maximum Dilatation		%	75	76
Initial Softening Temperature		°C	375	377
Maximum Contraction Temperature		°C	417	416
Maximum Dilatation Temperature		°C	463	461
EXTRA ANALYSIS				
Maximum Dilatation, D2.5	ASTM5515	%	85	96
Total Dilatation (%C + % D)	ISO 8264	%	100	101
Total Dilatation (%C + % D2.5)	ASTM D5515	%	110	121
MOISTURE				
Total Moisture	(TM) ASTM D3303	%	7.63	7.96
Residual Moisture	(RM) ASTM D3173	%	0.70	0.71

Case Study 2. Car Topper Dust Suppressant - 2nd Generation

Key concerns: change in polymer & wetting package

- Not as much positive impact on BD,
- Increase in Max Fluidity, but not temperatures/plastic range.
- Increase in Max Dilatation, total dilatation but not temperatures
- Quite different from 1st Generation despite minimal differences.
- Overall still within acceptable limits.

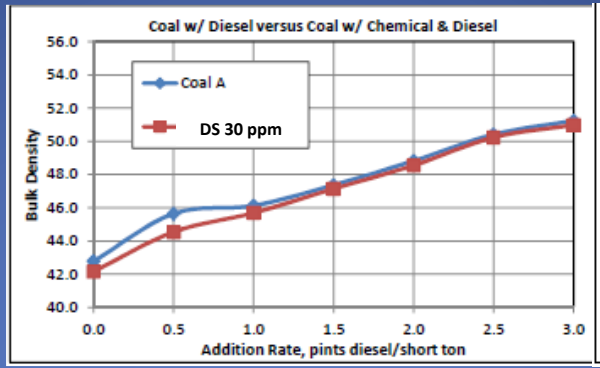


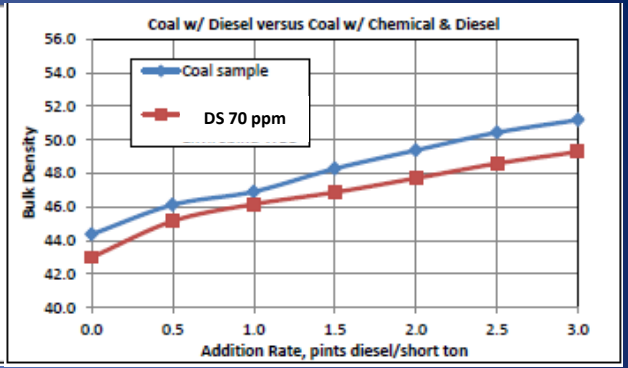
			Coal A	Coal A v Prod. X
GIESELER PLASTOMETER				
Maximum Fluidity	ASTM D2639	D.D.P.M.	588	645
Temperature at Maximum Fluidity		°C	458	457
Initial Softening Temperature (DDPM)		°C	417	416
Final Fluid Temperature		°C	490	489
Plastic Range		°C	76	75
Solidification Temperature		°C	493	491
AUDIBERT - ARNU DILATOMETER				
Maximum Contraction	ASTM D5515-97	%	25	23
Maximum Dilatation		%	89	106
Initial Softening Temperature		°C	373	386
Maximum Contraction Temperature		°C	416	418
Maximum Dilatation Temperature		°C	459	462
EXTRA ANALYSIS				
Maximum Dilatation, D2.5	ASTM5515	%	101	118
Total Dilatation (%C + % D)	ISO 8264	%	114	129
Total Dilatation (%C + % D2.5)	ASTM D5515	%	126	141
MOISTURE				
Total Moisture	(TM) ASTM D3303	%	8.32	8.54
Residual Moisture	(RM) ASTM D3173	%	0.79	0.84

Case Study 3. Conveyed Dust Suppressant

Key concerns: coal surface character & bulk density impact.

- 30 ppm shows no discernible difference in BD or other tests.
- 70 ppm shows significant loss of BD, outside acceptable limits.
- Proceeded to test 50 ppm.



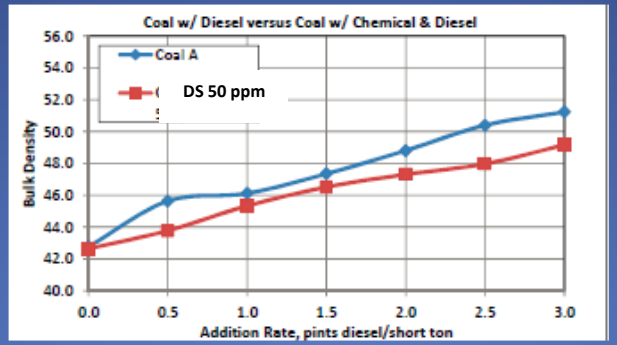


			Coal A	Coal DS 30 ppm
GIESELER PLASTOMETER				
Maximum Fluidity	ASTM D2639	D.D.P.M.	533	537
Temperature at Maximum Fluidity		oC	453	452
Initial Softening Temperature (DDPM)		oC	413	413
Final Fluid Temperature		oC	484	482
Plastic Range		oC	73	72
Solidification Temperature		oC	486	485
AUDIBERT - ARNU DILATOMETER				
Maximum Contraction	ASTM D5515-97	%	24	21
Maximum Dilatation		%	101	96
Initial Softening Temperature		°C	371	373
Maximum Contraction Temperature		°C	413	416
Maximum Dilatation Temperature		°C	455	457
EXTRA ANALYSIS				
Maximum Dilatation, D2.5	ASTM5515	%	122	112
Total Dilatation (%C + % D)	ISO 8264	%	125	117
Total Dilatation (%C + % D2.5)	ASTM D5515	%	146	133
MOISTURE				
Total Moisture	(TM) ASTM D3303	%	7.83	8.03
Residual Moisture	(RM) ASTM D3173	%	0.42	0.44

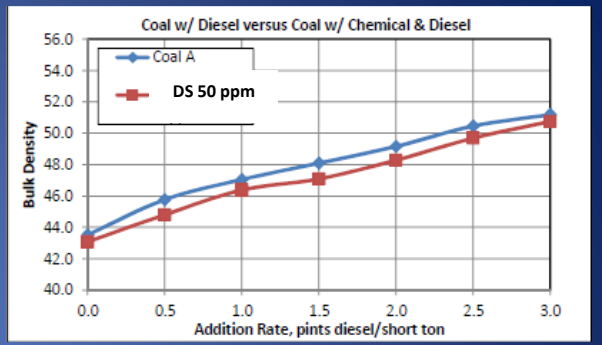
Case Study 3. Conveyed Dust Suppressant

Key concerns: BD and coke formation.

- Higher dosage impacts Max Fluidity and Dilatation negatively - significantly.
- Aging the sample reduced impact.
- Apparent that the active ingredients have a hard upper limit of 30-40 ppm.
- New technology required.



Freshly treated sample



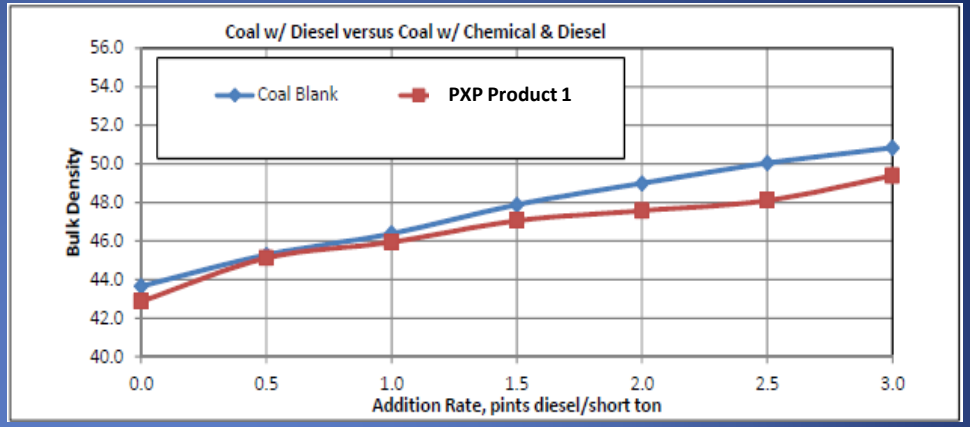
Aged for 3 weeks

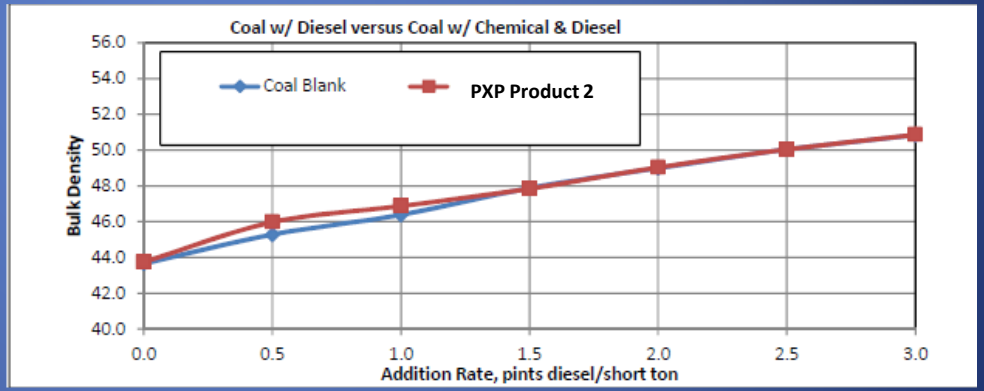
			Coal A	Coal A with DS 50 ppm
GIESELER PLASTOMETER				
Maximum Fluidity	ASTM D2639	D.D.P.M.	533	373
Temperature at Maximum Fluidity		°C	453	467
Initial Softening Temperature (DDPM)		°C	413	429
Final Fluid Temperature		°C	484	494
Plastic Range		°C	73	68
Solidification Temperature		°C	486	497
AUDIBERT - ARNU DILATOMETER				
Maximum Contraction	ASTM D5515-97	%	24	37
Maximum Dilatation		%	101	65
Initial Softening Temperature		°C	371	373
Maximum Contraction Temperature		°C	413	415
Maximum Dilatation Temperature		°C	455	450
EXTRA ANALYSIS				
Maximum Dilatation, D2.5	ASTM5515	%	122	84
Total Dilatation (%C + % D)	ISO 8264	%	125	92
Total Dilatation (%C + % D2.5)	ASTM D5515	%	146	111
MOISTURE				
Total Moisture	(TM) ASTM D3303	%	7.83	7.96
Residual Moisture	(RM) ASTM D3173	%	0.42	0.61

Case Study 3. Conveyed Dust Suppressant

Reformulation to avoid impact on coke quality:

- Changing surface interaction,
- Understand impact on diesel wetting.
- Different molecules to reduce impact on fluidity and dilatation.
- Product 2 was selected to move forward with.

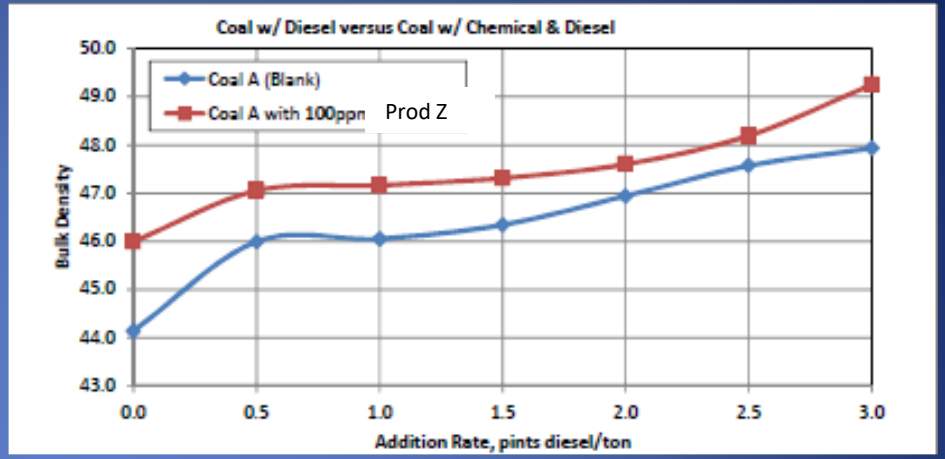


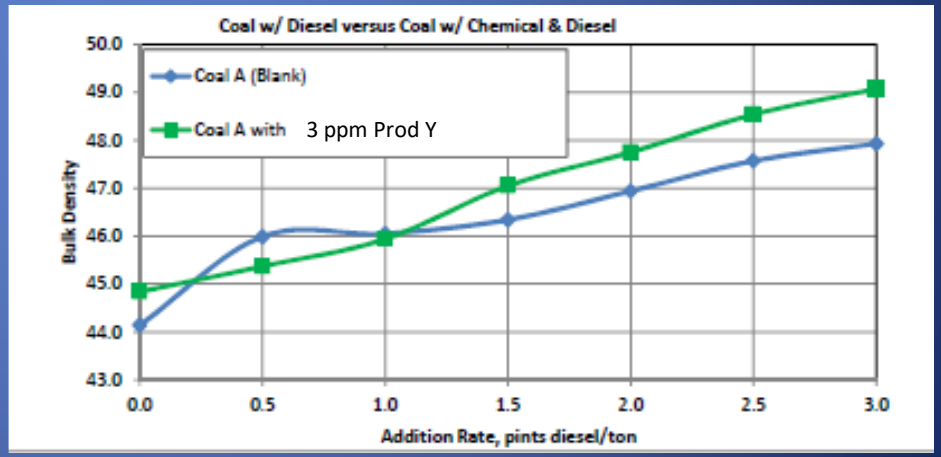


Case Study 4. Flowability Aids

Key concerns: 1) bulk density

- One product improves BD, one negatively affects BD at low diesel rates.
- Dosage 30X higher with positive effect.





Case Study 4. Flowability Aids

Key concerns:

- Fluidity,
- Dilatation
- Max. Dilatation

- Two different materials, two very different impacts.
- PXP3137 not viable.

			Coal A (Blank)	Coal w Prod Z 100 ppm	Coal w Prod Y 3 ppm
GIESELER PLASTOMETER					
Maximum Fluidity	ASTM D2639	D.D.P.M.	216	201	158
Temperature at Maximum Fluidity		°C	462	461	463
Initial Softening Temperature (DDPM)		°C	430	428	430
Final Fluid Temperature		°C	490	490	489
Plastic Range		°C	63	65	62
Solidification Temperature		°C	493	493	492
AUDIBERT - ARNU DILATOMETER					
Maximum Contraction	ASTM D5515-97	%	24	22	20
Maximum Dilatation		%	15	18	9
Initial Softening Temperature		°C	384	386	386
Maximum Contraction Temperature		°C	434	435	438
Maximum Dilatation Temperature		°C	465	468	466
EXTRA ANALYSIS					
Maximum Dilatation, D2.5	ASTM 5515	%	21	24	12
Total Dilatation (%C + % D)	ISO 8264	%	39	40	29
Total Dilatation (%C + % D2.5)	ASTM D5515	%	45	46	32

			Coal A (Blank)	Coal w Prod Z 200 ppm
GIESELER PLASTOMETER				
Maximum Fluidity	ASTM D2639	D.D.P.M.	83	120
Temperature at Maximum Fluidity		°C	464	464
Initial Softening Temperature (DDPM)		°C	435	431
Final Fluid Temperature		°C	490	491
Plastic Range		°C	58	63
Solidification Temperature		°C	493	494
AUDIBERT - ARNU DILATOMETER				
Maximum Contraction	ASTM D5515-97	%	20	20
Maximum Dilatation		%	8	5
Initial Softening Temperature		°C	391	388
Maximum Contraction Temperature		°C	439	440
Maximum Dilatation Temperature		°C	470	471
EXTRA ANALYSIS				
Maximum Dilatation, D2.5	ASTM 5515	%	15	12
Total Dilatation (%C + % D)	ISO 8264	%	28	25
Total Dilatation (%C + % D2.5)	ASTM D5515	%	35	32

Case Study 4. Flowability Aid

Key concerns:

- **Moisture addition**
- **Fluorine**
- **Chlorine**
- **No difference.**

Control

PROXIMATE ANALYSIS	Method	As Received
Moisture, Total %	ASTM D3302	5.69

MISCELLANEOUS ANALYSIS	Method	Dry
Chlorine, Cl ppm	ASTM D6721	<10
Fluorine, F µg/g	ASTM D3761	100

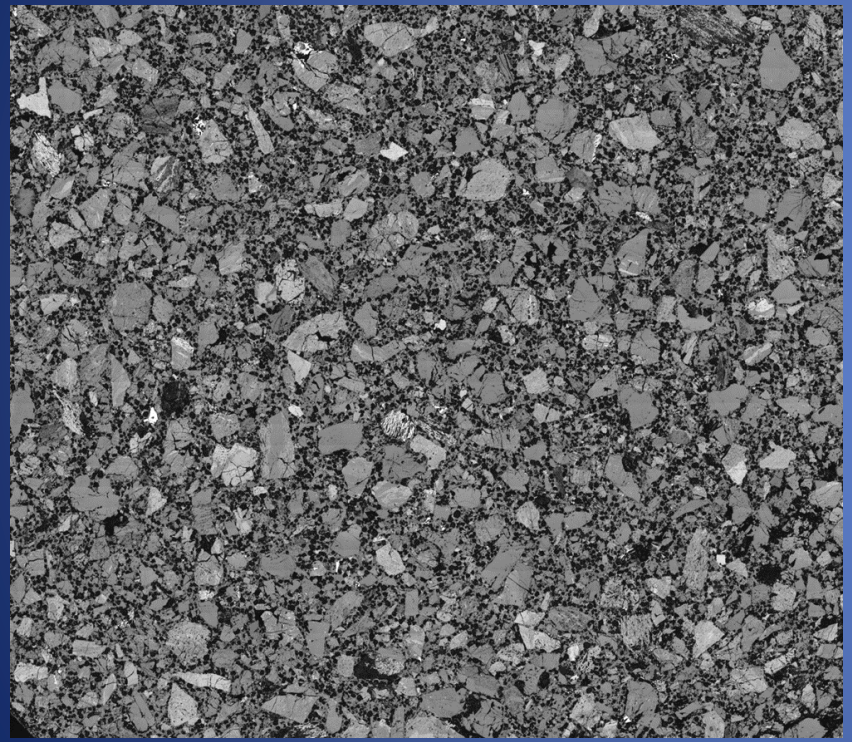
Coal with PFC

PROXIMATE ANALYSIS	Method	As Received
Moisture, Total %	ASTM D3302	5.57

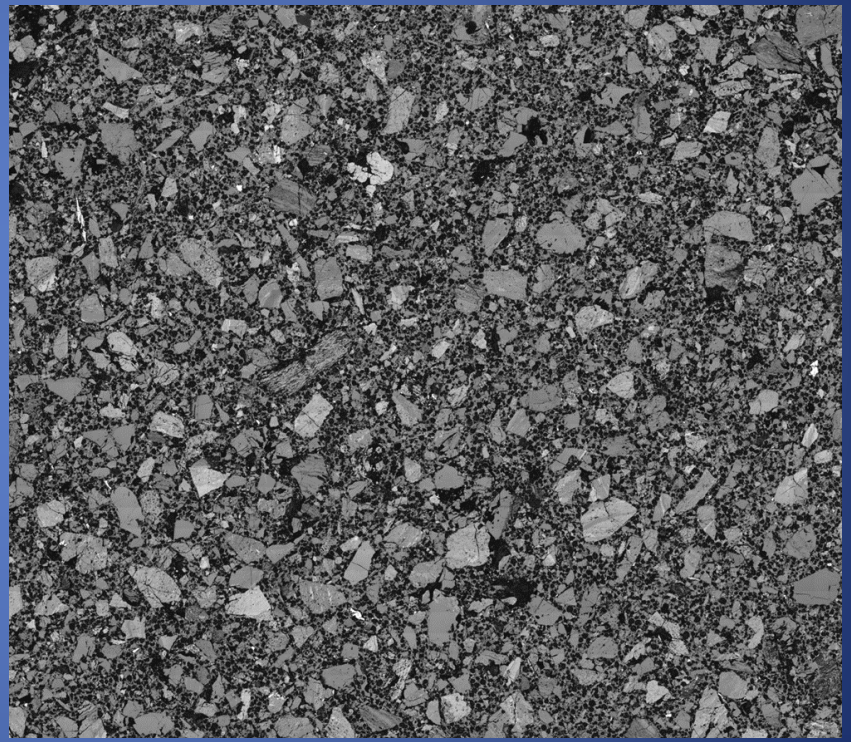
MISCELLANEOUS ANALYSIS	Method	Dry
Chlorine, Cl ppm	ASTM D6721	<10
Fluorine, F µg/g	ASTM D3761	100

Case Study 4. Flowability Aid

Key concerns: Petrography



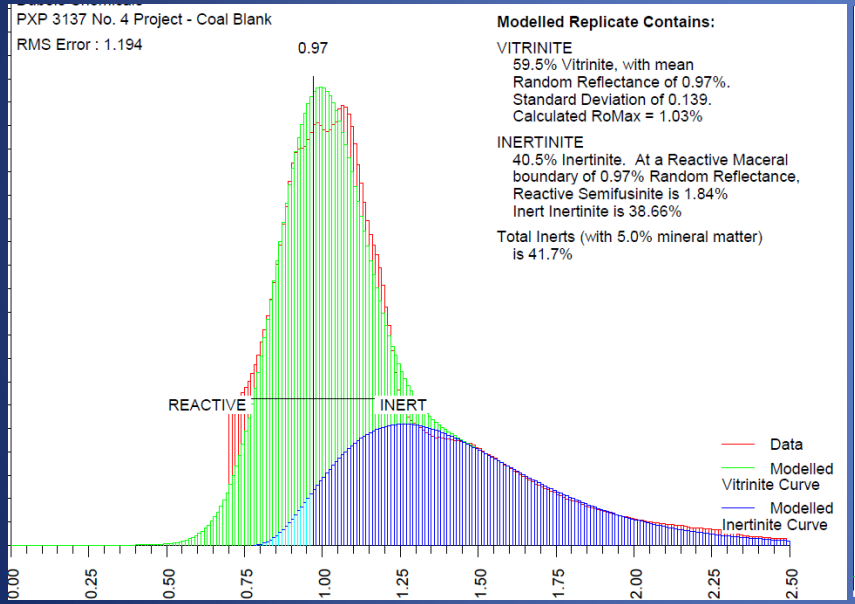
Untreated



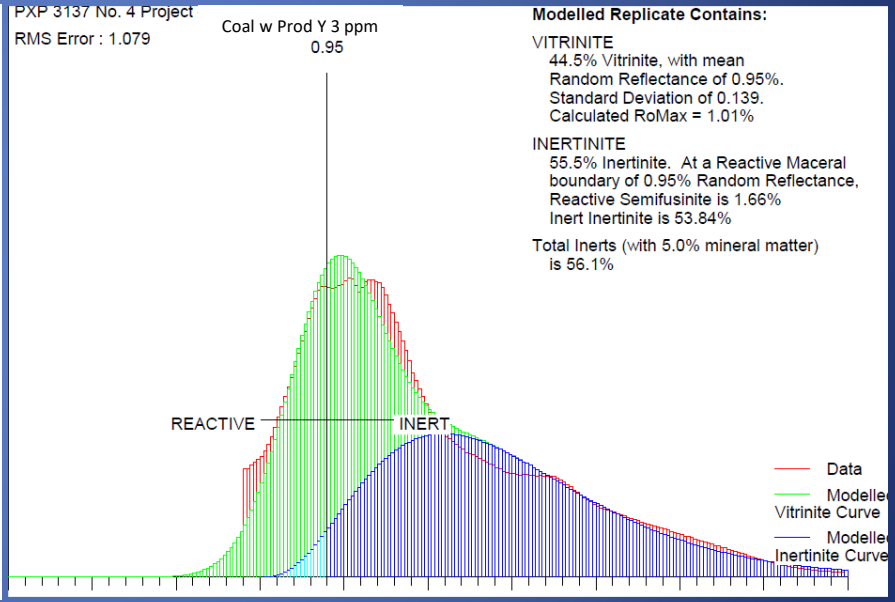
Treated with Prod Z

Case Study 4. Flowability Aid

Key concerns: Petrography



Untreated



Treated with PFC

HCC COKE IMPACTS: SUMMARY

- Some predictions for impact are straightforward, others are not!
- The process for additive evaluation is lengthy, but is a stepwise, logical progression required to ensure the high quality of Canadian coal is preserved.
- Understanding how additives may impact the myriad coke properties allows for product development and dosage management.
- New technologies are not predictable, therefore testing is imperative.
- Performance test screening and elemental analysis conducted prior to Coke Impact testing highly recommended.

Thank you:

- **Teck Resources**
- **Intertek**
- **SGS**
- **Pearson Petrography**
- **Dubois Technical Team**

Questions and Follow up

Chris Burke
DuBois Chemicals Canada
Resource RSM APAC/Americas
chris.burke@duboischemicals.com
1670 W. 75th Avenue
Vancouver, BC Canada