Pittsburgh Mining Research Division

Rock Dust Partnership Meeting

December 5, 2017

Agenda

Welcoming Comments

Opening Comments

NIOSH – Progress to Date

- NIOSH Health Effects Laboratory Division
- NIOSH Pittsburgh Mining Research Division

Comments and Discussion – Future efforts

Concluding Comments

Opening comments

- NIOSH – Dr. Jessica Kogel & Dr. R.J. Matetic
- MSHA – Stan Michalek
- IMA-NA – Mark Ellis
- NSSGA – Emily Coyner
- NLA – Hunter Prillaman/Bradford Frisby
- NMA – Bruce Watzman
- BCOA – Ed Green
- UMWA – Josh Roberts

Action Items from Last Meeting

- Silica and toxicity data
- Engineered rock dust
- In-mine studies
- Foamed rock dust

Initial Partnership

Inconsistencies in available rock dust supply

- Particle sizing
- Dispersibility

Rock Dust Partnership

- IMA-NA
- NSSGA
- National Lime Assoc.
- MSHA

Test methods to assess rock dust quality

Improving rock dust performance

Expanded Partnership

Potential health effects

- Respirable silica
- Toxicological

Perceived respirable dust issues

Industry

- National Mining Assoc.
- Bituminous Coal Operators Assoc.

Labor

- United Mine Workers of America

NIOSH Mining – Progress to Date

- Rock dust toxicity – NIOSH/HELD
- Large scale testing at Polish Central Mining Institute
- Wrap-up of engineered rock dust
- Foamed rock dust work

Rock Dust Toxicity

Toxicity Studies of Rock Dust Samples. (*In vitro Assessments*)

Dr. Anna A. Shvedova
NIOSH / HELD

Dec 5th 2017

What Do We Know about Health Outcomes Elicited by Calcium Carbonate Dust ?

- Eight cases of suspected pneumoconiosis following inhalation of limestone dust with low silica content were described by Doig et al. (1953).
- Granulomatous lesions containing limestone particulates were reported in lungs of quarry worker (Crummy et al. 2004).
- Limestone quarry workers had increased prevalence of respiratory symptoms, e.g. various coughs, wheezing and shortness of breath (Bwayla et al. 2011).
- Pulmonary alveolar proteinosis observed in marble-cutter in Turkey (Case study: Yildirim et al. 2015).
- Erasmus syndrome (pneumoconiosis) in marble worker, most likely exposed to high silica concentrations (Bello et al. 2015).

What Do We Know about Health Outcomes Elicited by Calcium Carbonate Dust ?

- Increased IL-8 level (inflammation marker) in serum was associated with limestone dust concentration and the duration of exposure in limestone miners (Tolinggi et al. 2014)

- Calcium carbonate dusts are not considered fibrogenic dusts, but rather irritants (NIOSH guideline, 1995).

- Co-exposure with silica is most likely responsible for COPD, pneumoconiosis and fibrosis seen in limestone/marble workers:

    - Even though the level of silica is very low – it may still cause the adverse outcomes in susceptible individuals (Doig et al., 1954, Crummy et al. 2004, Angotzi et al. 2005).

Need for Developing Anti-caking Rock Dust

Coating with hydrophobic Stearate

- Limestone-based rock dusts are used to prevent explosions caused by high coal dust content in the air.

- Treating limestone will provide better dispersion of the materials.
  - Under humid conditions, limestone-based rock dusts have a tendency to cake.

- Treated limestone particles can fill the empty spaces between the larger untreated limestone particles, preventing or inhibiting the migration of water throughout the blend.

Need for Developing Anti-Caking Rock Dust

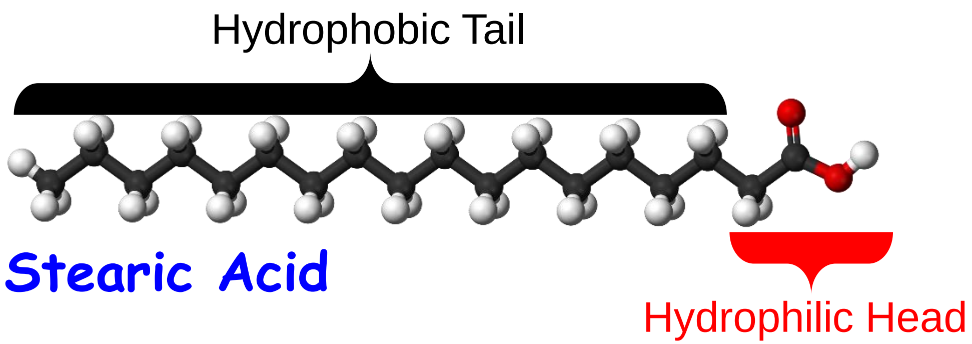
NIOSH 2014 Study

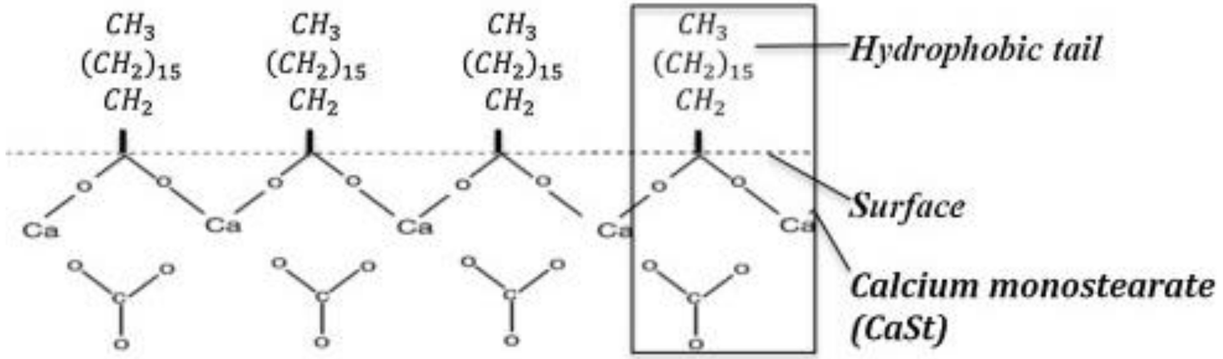
- **Objective:** To develop modified limestone based rock dust blend(s) that are capable of :
  - Effectively dispersing (NIOSH dust dispersion chamber after being wetted, then dried)
  - Increasing the inertness of coal dust (NIOSH 20-L explosibility chamber).

- **Recommendations:** 20 – 25 μm untreated rock dust blended with 10% + 2.5% of a 3 μm treated component (e.g., stearate).

Anti-Caking Rock Dust

Treatment Details





Cao, Z. et al., 2016

During the treatment, stearic acid is adsorbed on the surface of $CaCO_3$ particles by covalent bond between the stearic acid "head" group and Ca^{2+}, forming a monolayer of hydrophobic molecules.

Particle Characterization

Representative TEM images of respirable rock dust

Particles Investigated in the Current Study

UL

- Untreated Limestone

TL

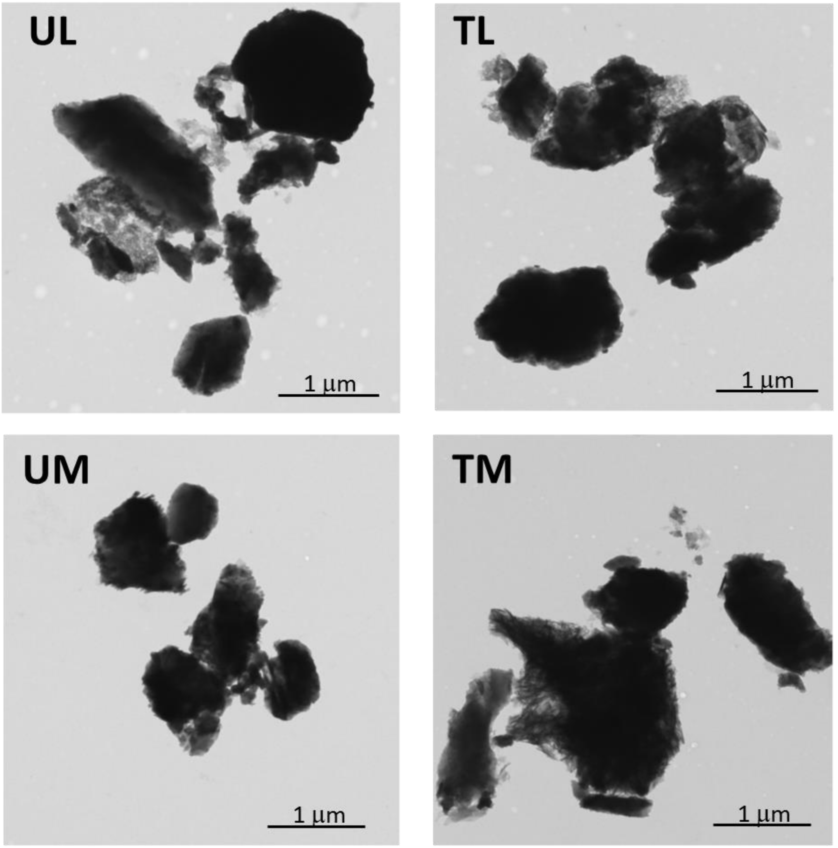
- Treated Limestone

UM

- Untreated Marble

TM

- Treated Marble

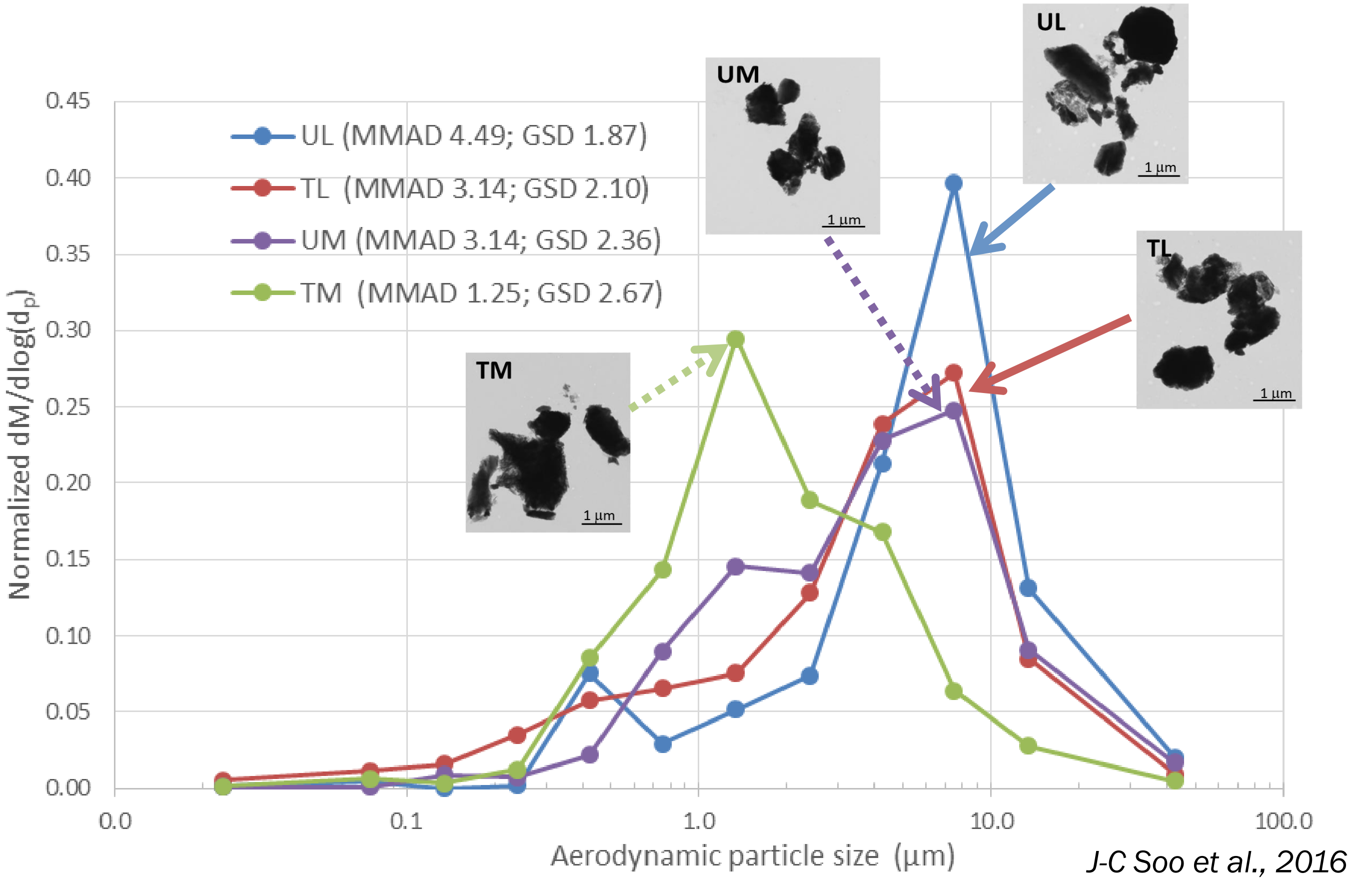


J-C Soo et al., 2016

Details of Collection: Respirable fractions of rock dusts were collected with FSP10 cyclones loaded with polyvinyl chloride filters (PVC, 5 µm pore size, 37 mm). The collected particles on PVC filters were washed with a mix of phosphate buffered saline and isopropyl alcohol. Then samples were centrifuged and dried.

Particle Characterization

Aerodynamic particle size distribution of airborne rock dust



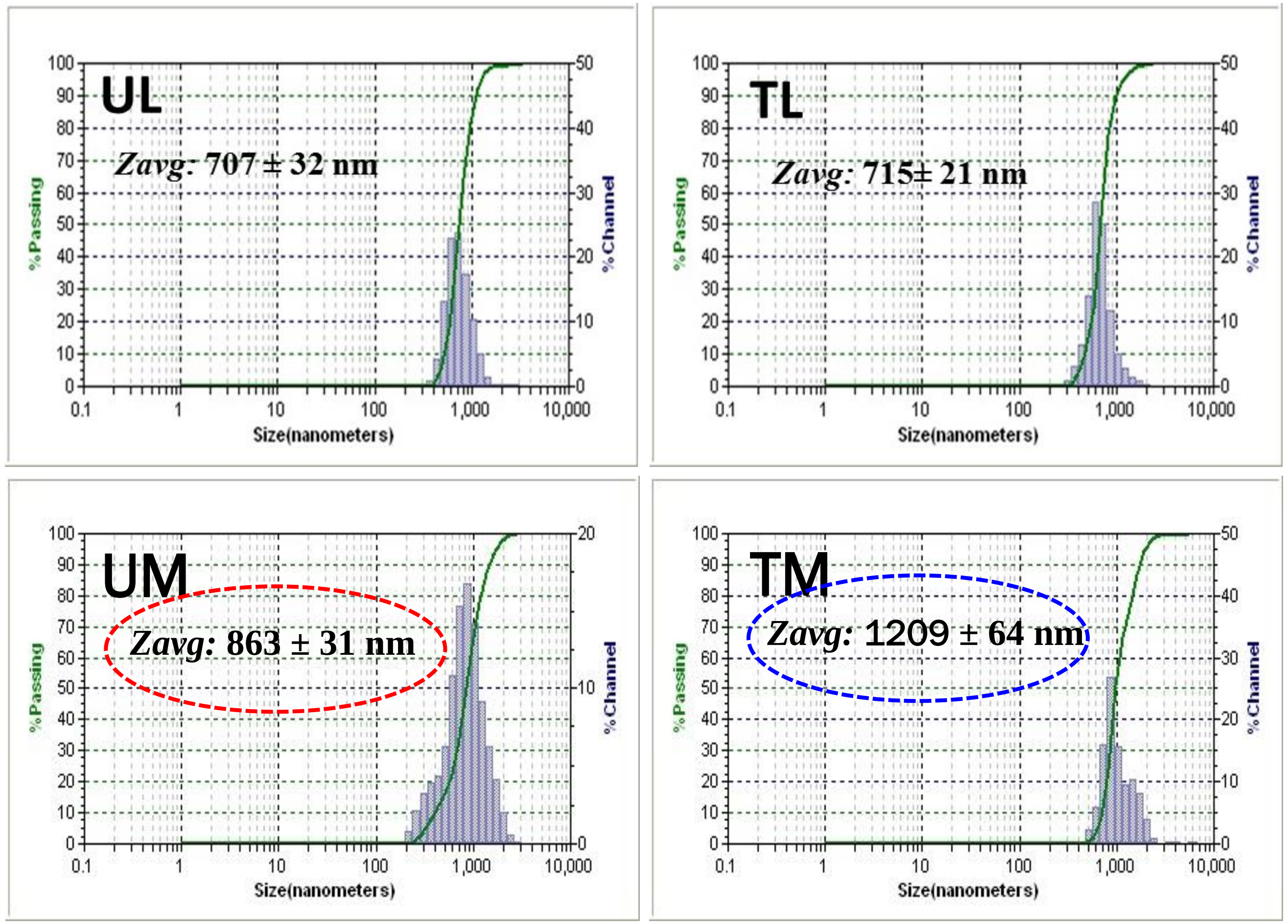
J-C Soo et al., 2016

Respirable fractions of rock dusts were collected with FSP10 cyclones loaded with polyvinyl chloride filters (PVC, 5 µm pore size, 37 mm). The collected particles on PVC filters were washed with a mix of phosphate buffered saline and isopropyl alcohol. Then samples were centrifuged and dried.

The mass median aerodynamic diameter (MMAD) of treated marble (TM) sample is lowest compared to other rock dust samples investigated.

Particle Characterization

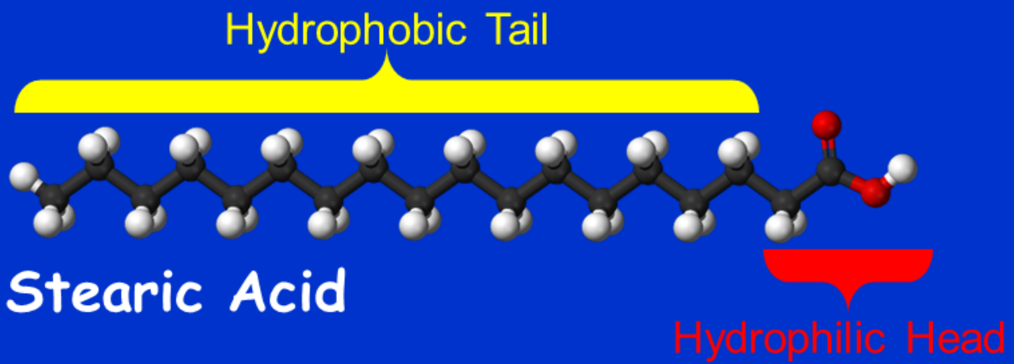
Average hydrodynamic diameter of respirable fraction of rock dust



The average size/distribution of rock dust samples were determined using DLS measurements. The hydrodynamic diameter (Zavg) from DLS were represented as mean ± SD. The reported Zavg values correspond to a mean of six different measurements.

The average size of treated marble (TM) rock dust sample was higher compared to other rock dust samples investigated.

Hydrodynamic size measured of treated marble by DLS is highest between all samples. Since the DLS measurements were in aqueous solution – could it be due to the agglomeration of treated rock dust (through hydrophobic surfaces)?



Stearic Acid

Other Particles: What we have seen?

Uncoated and Lignin-coated Nanocellulose Crystals and Fibers.

Particle Characterization

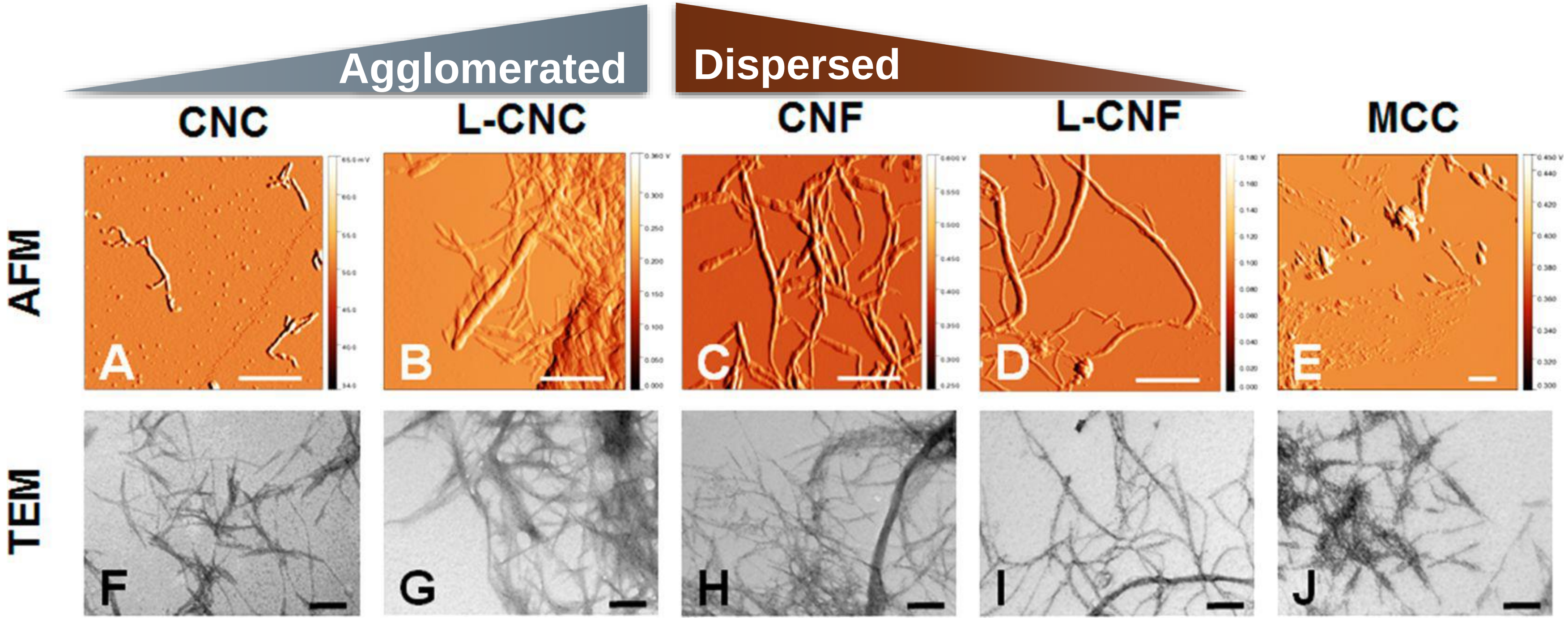


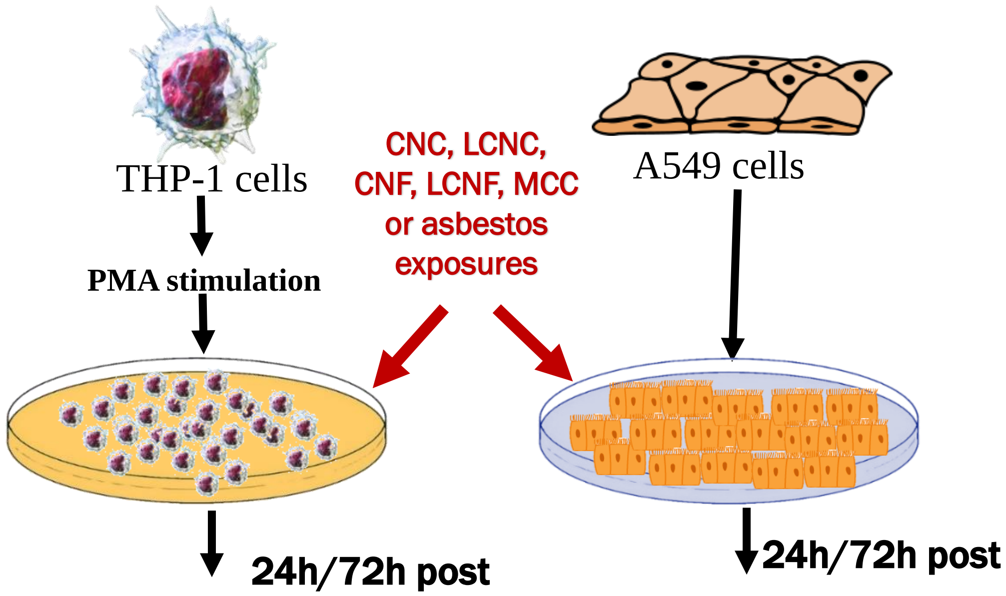
Figure: Characterization of nanocrystalline and microcrystalline cellulose samples. (A−E) AFM amplitude and (F-J) TEM images of CNC (A,F), L-CNC (B,G), CNF (C,H), L-CNF (D, I) and MCC (E,J). Scale bar in all AFM and TEM images corresponds to 500 nm and 200 nm, respectively.

Depending on the cellulose nanomaterial type and/or its morphology, lignin coating can lead to differential agglomeration/aggregation influencing their physicochemical properties in aqueous media.

Other Particles: Toxicity Evaluation

Uncoated and Lignin-coated Nanocellulose Crystals and Fibers.

Experimental Details

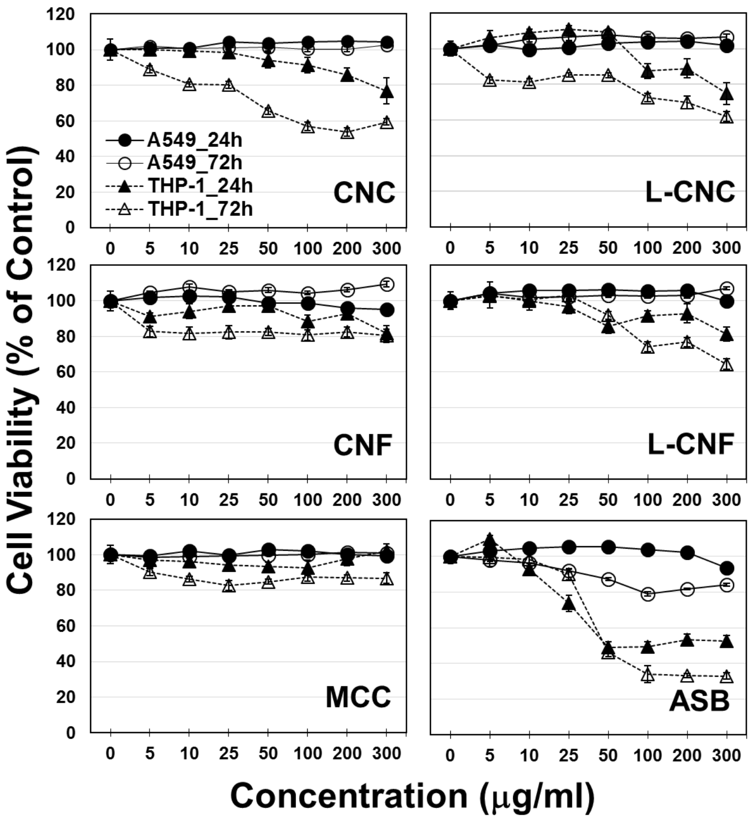


Cellular Viability

Inflammatory cytokines/chemokines

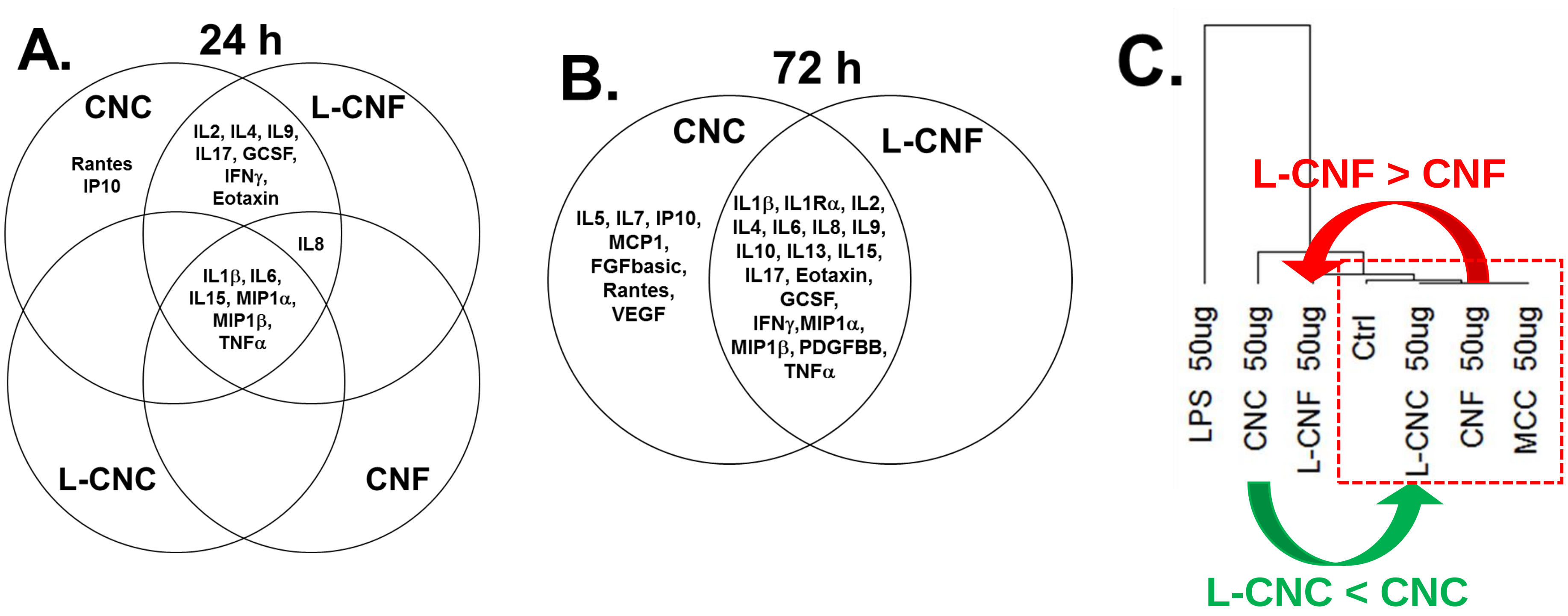
(Human 27-plex kit from Bio-RAD)

Viability Responses



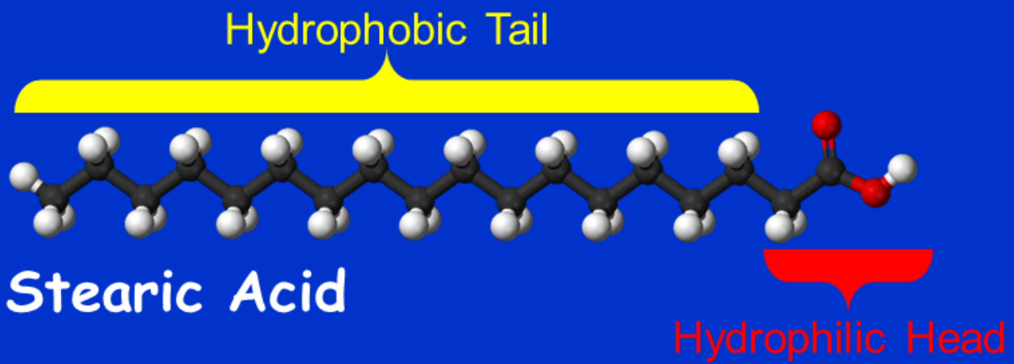
Other Particles: Toxicity Evaluation

Inflammatory Cytokine Responses



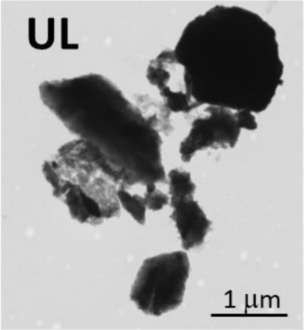
The overall inflammatory responses in cells upon exposure to various concentrations of different NC materials investigated were in the order: CNC > L-CNF > CNF ≥ L-CNC ≥ MCC.

Does Exposure to Different Rock Dust Samples Trigger Variable Biological Responses *In Vitro*? If so, what is the effect of treatment with stearic acid?



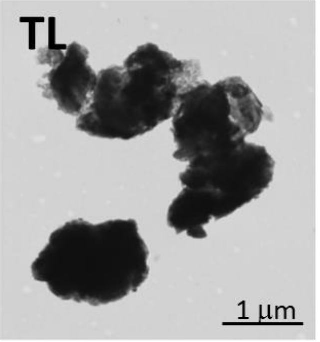
In vitro Evidence for Discriminating between different Respirable Rock Dust

Similar Approach as Nanocellulose Materials



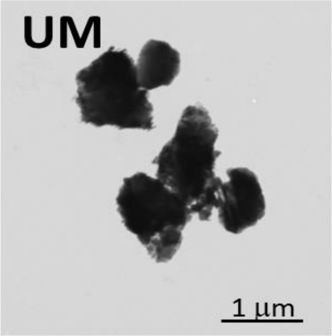
Untreated Limestone

(or)



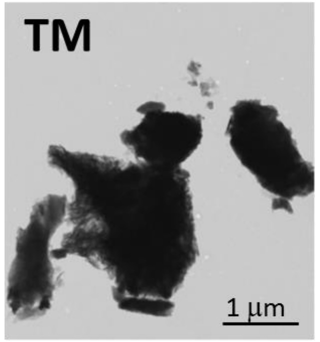
Treated Limestone

(or)

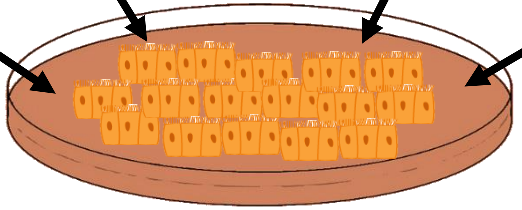


Untreated Marble

(or)



Treated Marble



A549
Human pulmonary alveolar epithelial cells

24h/72h

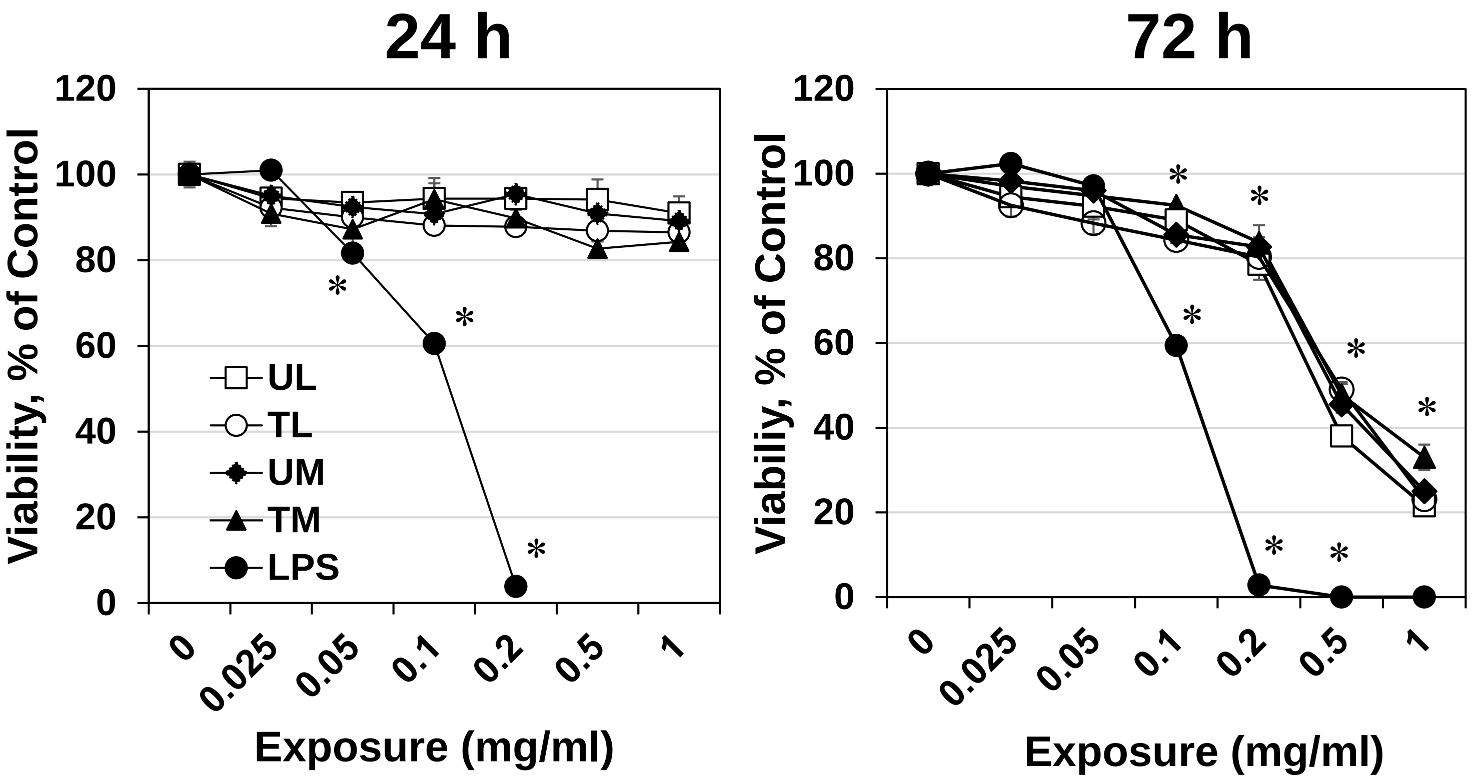
Particle Concentration's:

- 0 mg/ml
- 0.025 mg/ml
- 0.050 mg/ml
- 0.100 mg/ml
- 0.200 mg/ml
- 0.500 mg/ml
- 1.0 mg/ml

Cellular Viability/Damage
Inflammatory cytokines/chemokines
(human 27-plex kit from Bio-RAD)

In vitro Evidence for Discriminating between different Respirable Rock Dust

Cytotoxicity (viability) of various respirable rock dust samples

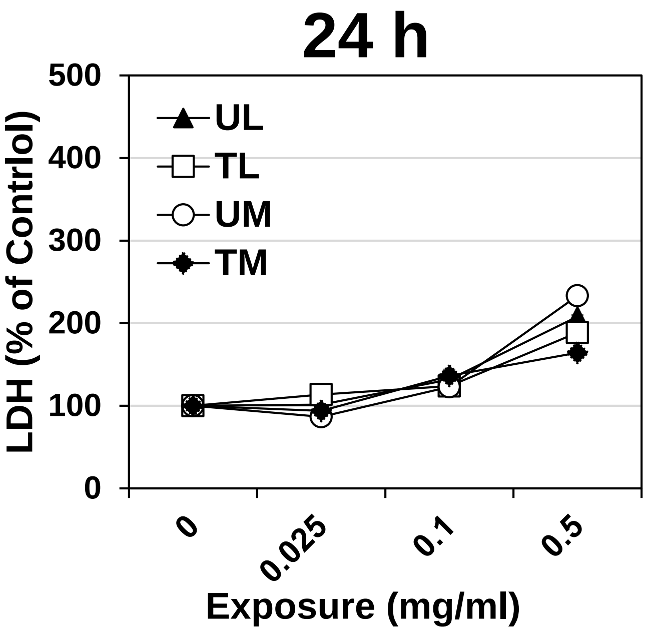


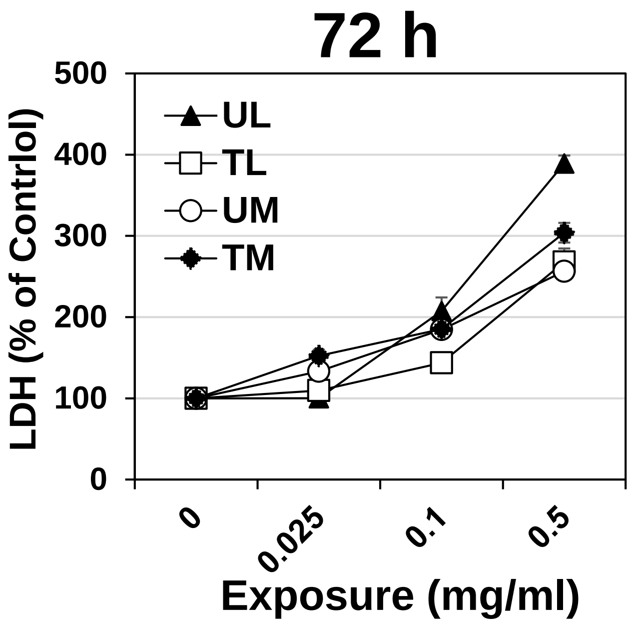
LC_{50} (mg/ml, 72h)	
UL	0.41
TL	0.49
UM	0.46
TM	0.48
LPS	0.108

A dose- and time-dependent cytotoxicity was observed in A549 cells upon exposure to different respirable rock dust samples.

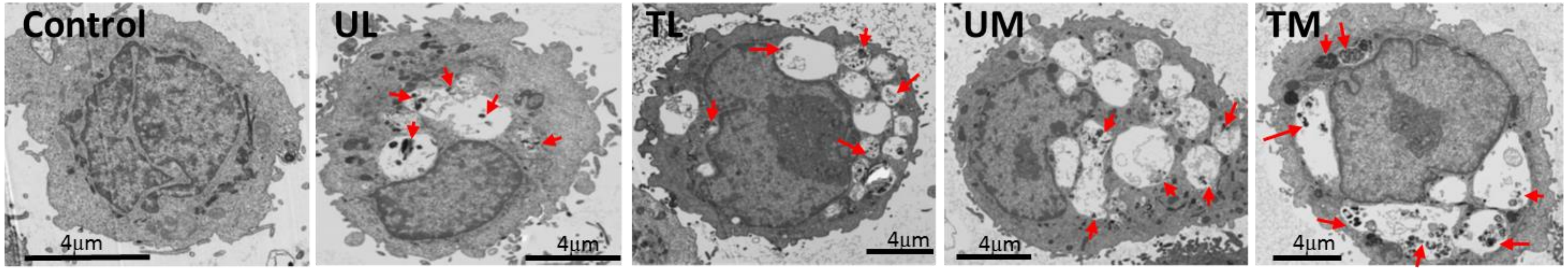
In vitro Evidence for Discriminating between different Respirable Rock Dust

Cytotoxicity (cell damage) of various respirable rock dust samples





Representative TEM macrographs of A549 cells exposed to respirable rock dust (72h, 0.1 mg/ml)



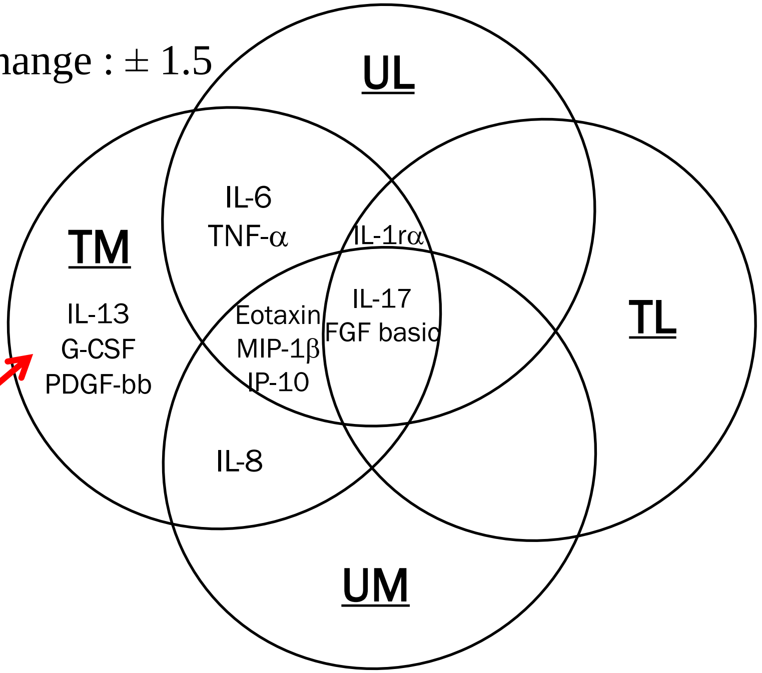
Red arrows indicating particle uptake.

In vitro Evidence for Discriminating between different Respirable Rock Dust

Inflammatory Cytokine/Chemokine Responses

A Venn diagram presenting the responses in inflammatory mediators upon exposure of A549 cells to respirable rock dusts (0.1 mg/ml) for 72h.

Fold Change : ± 1.5

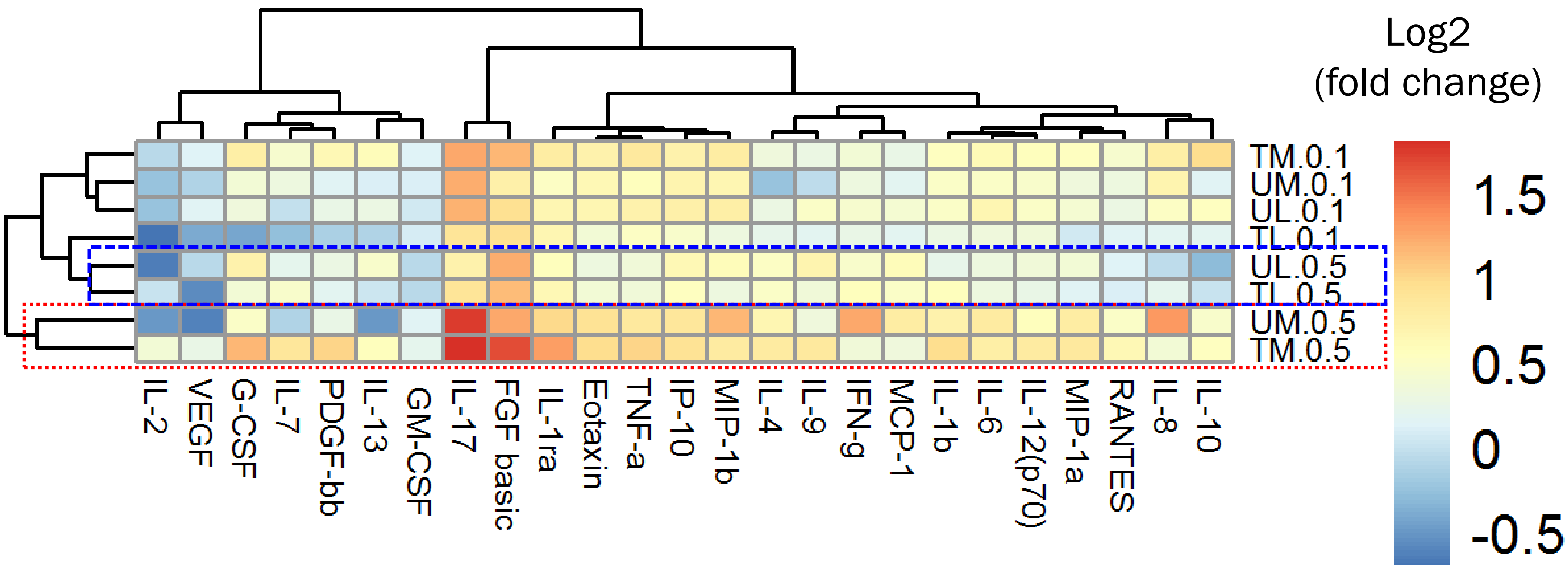


Some cytokines are unique to treated marble (TM) samples.

Treated limestone (TL) revealed the lowest inflammatory response compared to other rock dust samples.

In vitro Evidence for Discriminating between different Respirable Rock Dust

Hierarchical cluster analysis of cytokine profiles in A549 cells after 72h



The samples of A549 cells exposed to different concentrations of rock dust for 72h were clustered based on the Euclidean distance metric and ward.D2 clustering method. The samples corresponding to different rock dust and several cytokines measured in supernatants were reordered based on their (dis-)similarities according to the dendrogram on the top and left, respectively. Each branch in the dendrogram shows the similarity between samples, i.e., the shorter the branch, the more similar. The heat map colors represent log2 transformed fold change values of cytokines relative to the minimum and maximum of all values, increasing from red to green, in each case. A key showing the range of values is also shown in the figure.

Clustering analysis of the inflammatory cytokines/chemokines revealed an overall stronger effect of marble compared to limestone samples. A clear separation of marble rock dust from limestone samples was also observed.

Summary

- The results showed a dose-dependent cytotoxicity and cell damage at 72 h in A549 cells, with the least effect upon exposure to treated limestone (TL).

- The extent of inflammatory responses evaluated by the number of cytokines released, increased with the concentration of tested materials.

- Clustering analysis of the inflammatory cytokines/chemokines revealed an overall stronger effect of marble (i.e., UM,TM) compared to limestone samples (i.e., UL,TL).

Summary (cont.…)

- Furthermore, untreated rock dust induced an overall greater inflammatory response as compared to treated samples.

- Similar to the cytotoxic and cell damage results, treated limestone (TL) revealed the lowest inflammatory response compared to other samples.

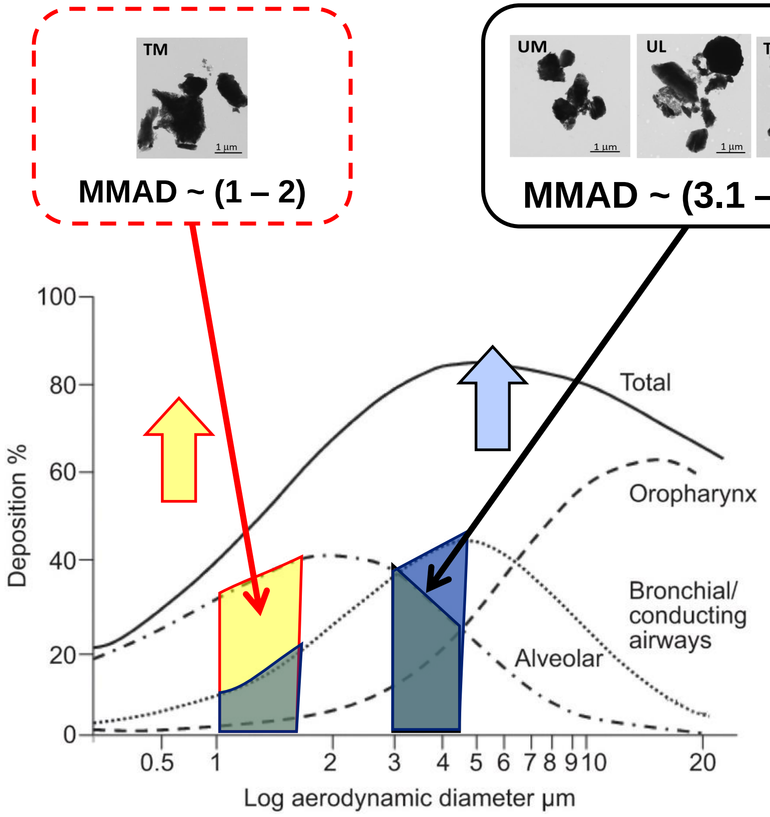
- Similar to what we have seen before in nanocellulose, treatment related differences between limestone (TL) and marble (TM) samples were observed.

Overall, our results unveiled treatment related differences as well as material dependent changes in biological responses.

Pulmonary Deposition

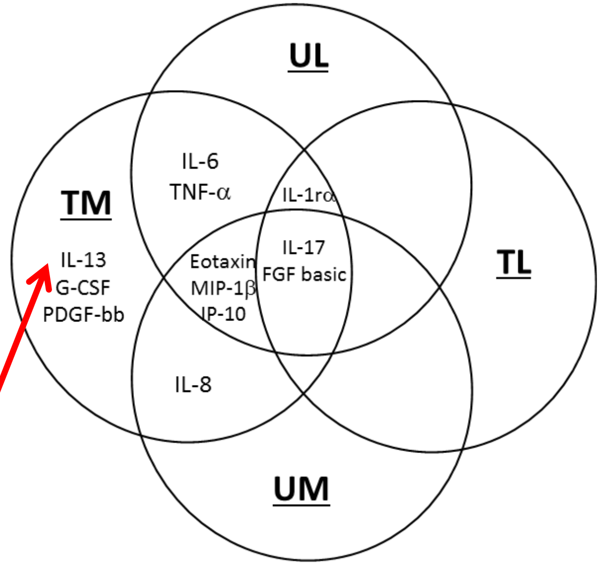
Respirable Rock Dust Samples

* **MMAD:** Mass Median Aerodynamic Diameter



Bronchial and Conducting Airways Deposition

Fold Change : ± 1.5



Under In vivo conditions, allergic immune responses are characterized by the production of IL-13 and other cytokines.

There is strong need for animal studies to adequately address pulmonary toxicity responses of (un-)treated rock dust.

Disclaimer: The findings and conclusions in this presentation are those of the authors and do not necessarily represent the views of the National Institute for Occupational Safety and Health. The mention of any company names or products does not imply an endorsement by NIOSH or the Centers for Disease Control and Prevention, nor does it imply that alternative products are unavailable, or unable to be substituted after appropriate evaluation.

Thanks To My Collaborators:

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S. Guppi
D. Weissman
M. Harper

Funding: ???

CDC Workplace Safety and Health

NIOSH

Large-Scale Testing

Large-scale Testing

Central Mining Institute Located in Mikołów, Poland

Personnel

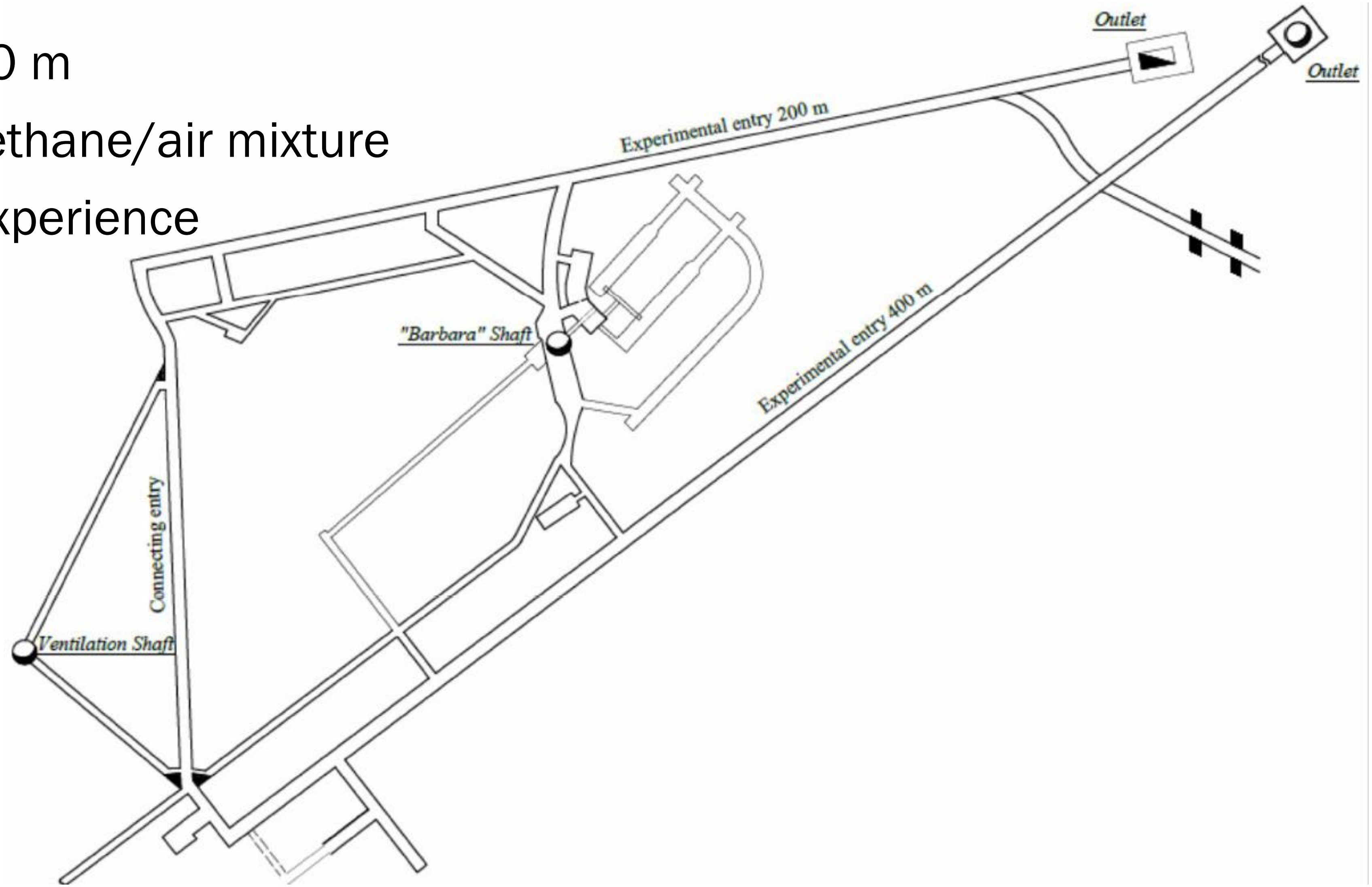
- Experimental Mine Barbara
- NIOSH PMRD

Objective

- To determine whether an anti-caking treatment would hinder the effectiveness of the rock dust

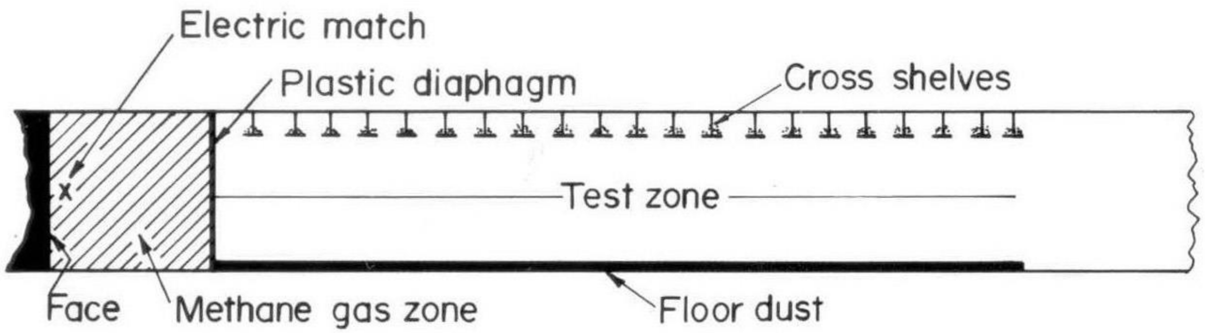
Why Poland?

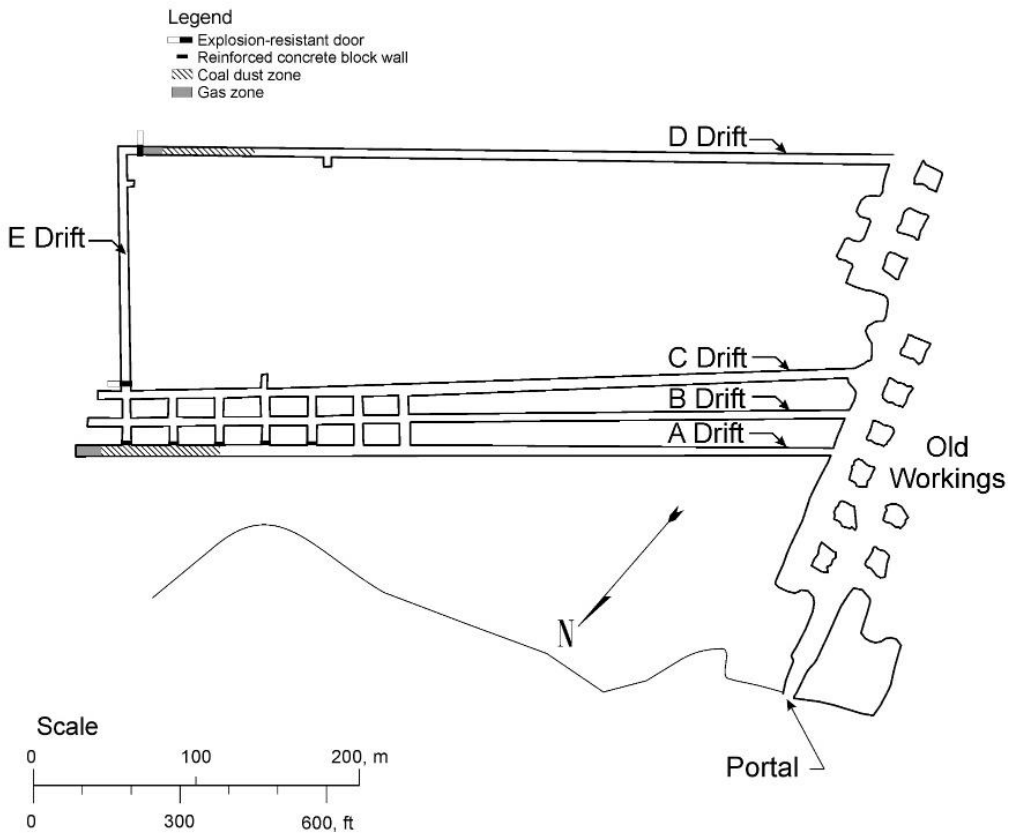
- Length of entry – 400 m
- Ignition method – methane/air mixture
- Testing history and experience

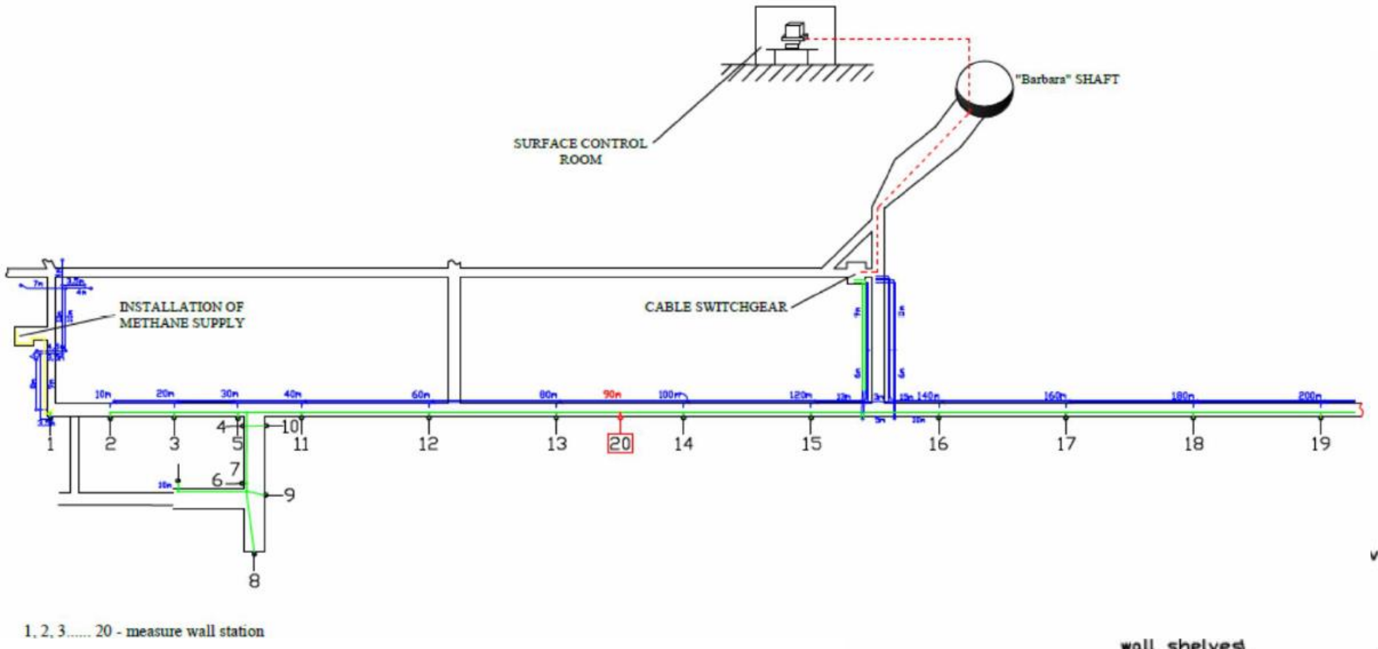


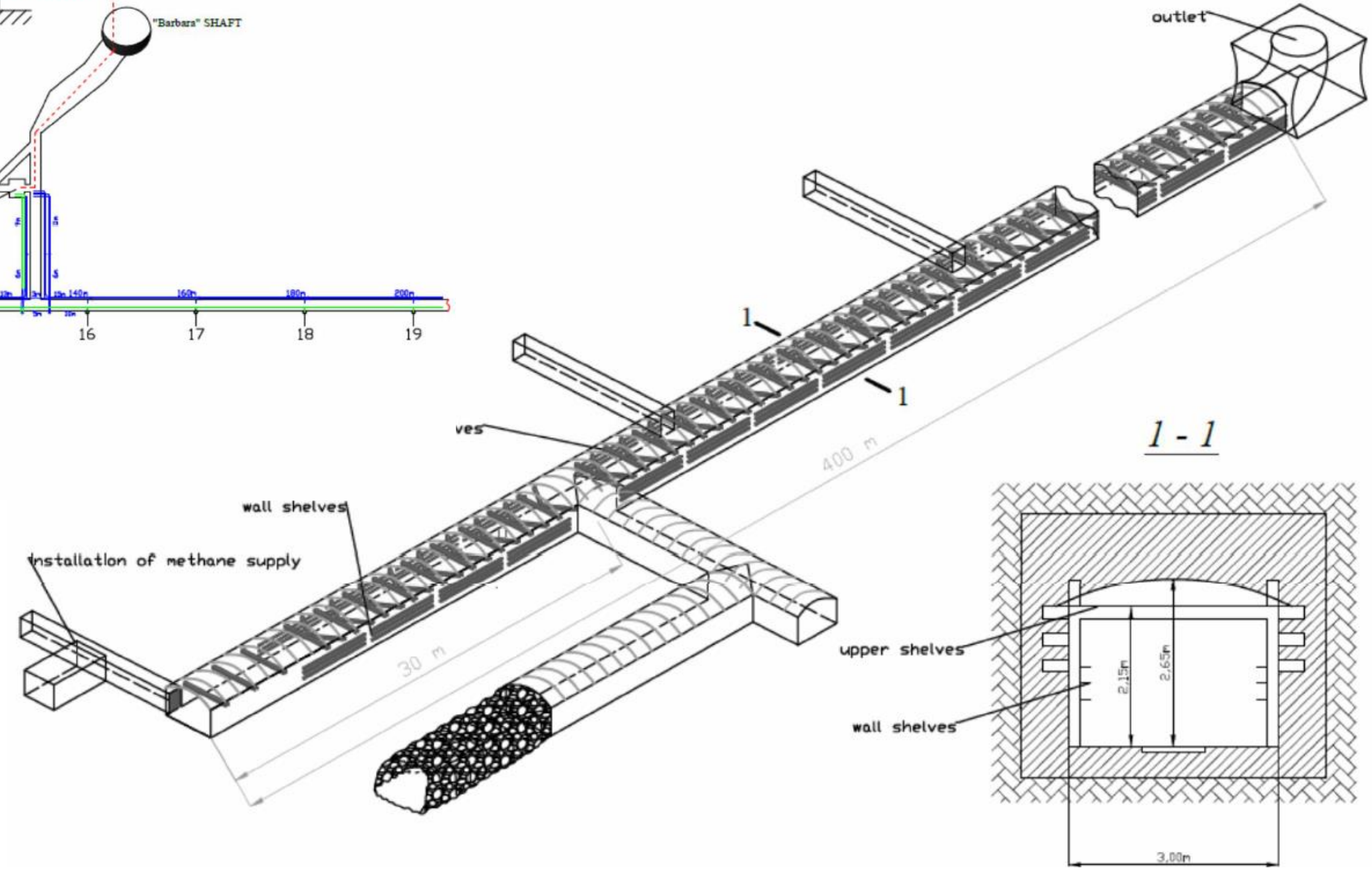
Lake Lynn Experimental Mine

- Length of entry – 490 m
- Ignition method – methane/air mixture

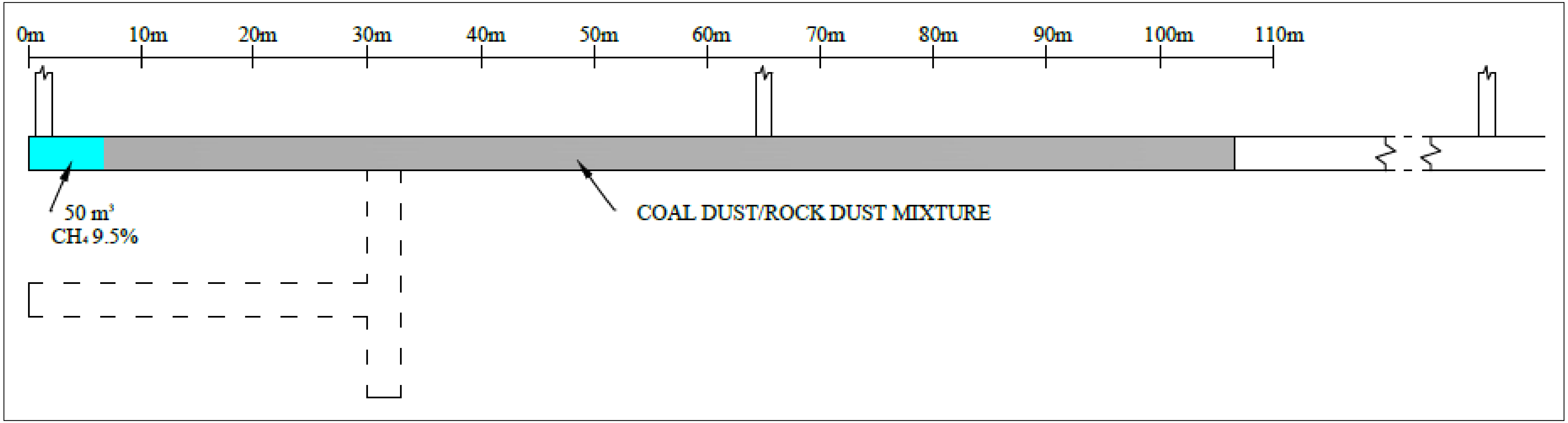





SURFACE CONTROL ROOM
"Barbara" SHAFT
INSTALLATION OF METHANE SUPPLY
CABLE SWITCHGEAR
1, 2, 3...... 20 - measure wall station


outlet
1
1
1 - 1
ves
400 m
wall shelves
installation of methane supply
30 m
upper shelves
wall shelves
2,15m
2,65m
3,00m

Test Setup



0m
10m
20m
30m
40m
50m
60m
70m
80m
90m
100m
110m
50 m³
CH₄ 9.5%
COAL DUST/ROCK DUST MIXTURE

Test Basis

Testing at EM Barbara was conducted on a comparative basis

- Shipment of dust to Poland
    - Estimates of $26,000/ton of material
- Insufficient d99 Polish coal dust for large-scale testing
- d38 coal dust ≈ medium coal dust (RI 9679)
- Polish rock dust ≈ Reference rock dust (RI 9679)

The Polish coal dust and the Pittsburgh coal have similar properties

	Pittsburgh Coal	Barbara d38
Moisture, %	1.7	2.9
Volatility,%	36.5	36.7
Ash, %	6.2	7.9

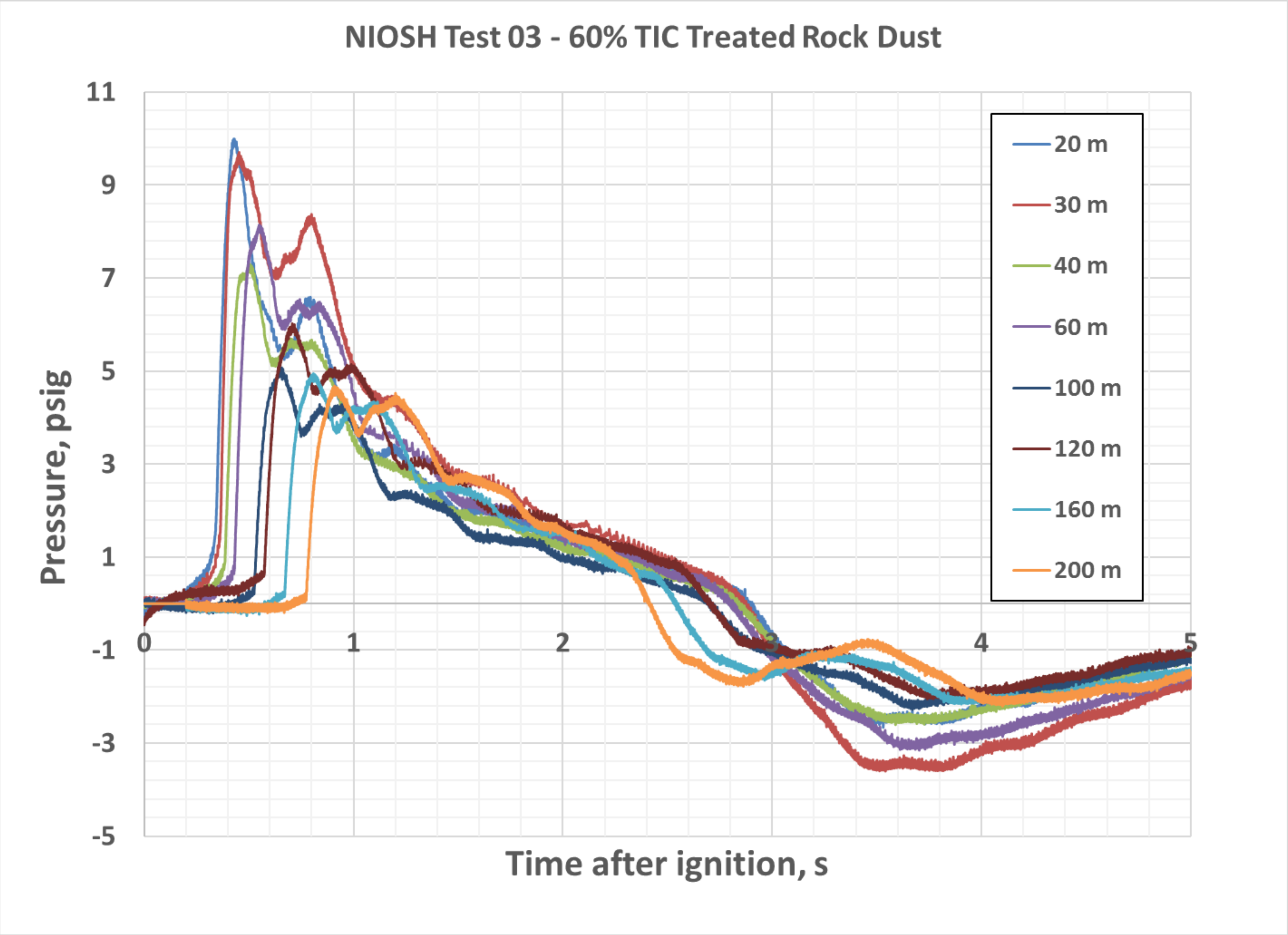
The Polish treated and untreated rock dusts perform similar to the Reference rock dust in the 20-L chamber

Rock Dust	Coal Dust	% Rock Dust Inerting	% TIC
Reference	d38 Polish	60	70.8
Polish untreated	d38 Polish	60	70.8
Polish treated	d38 Polish	60	70.8

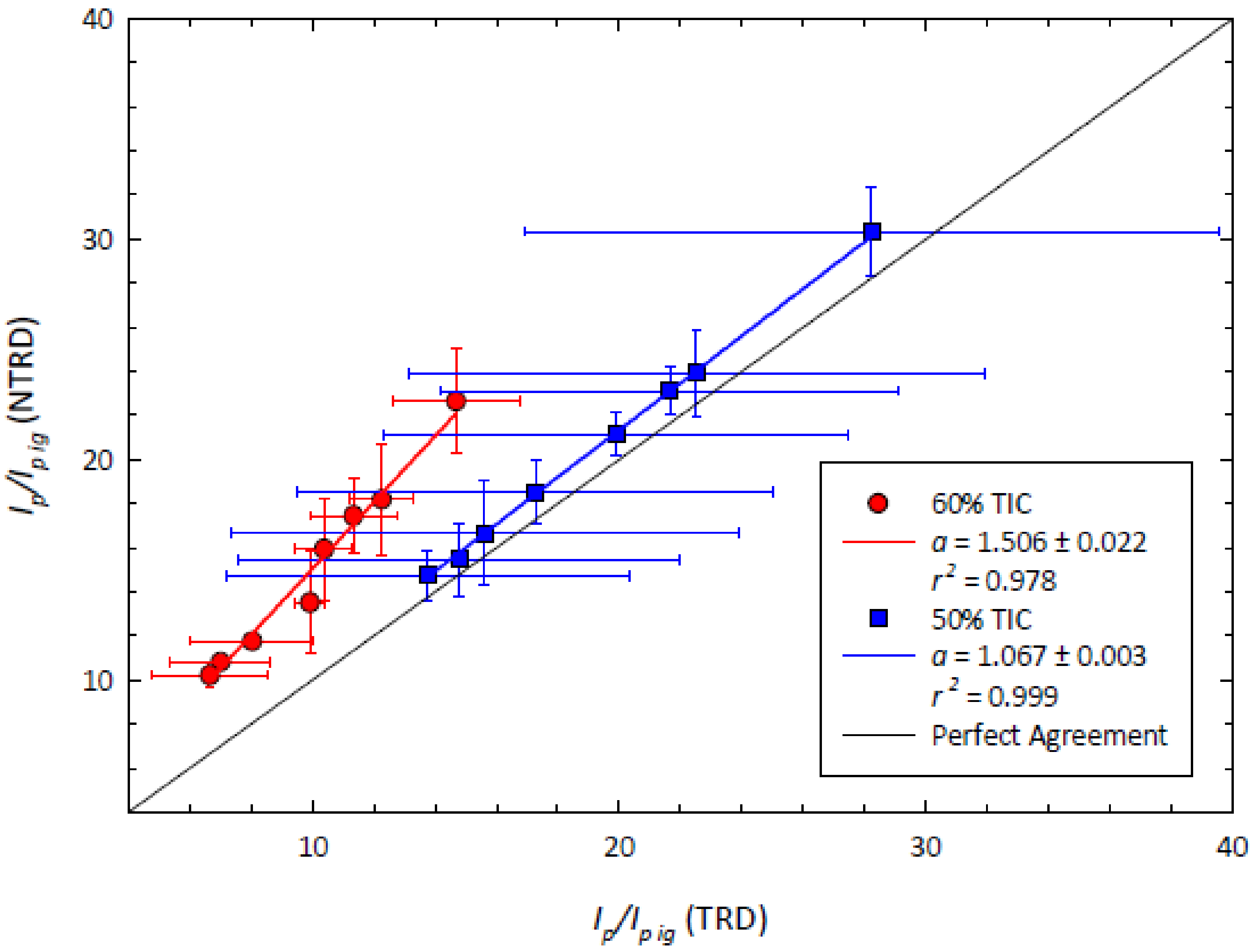
Tests conducted at EM Barbara

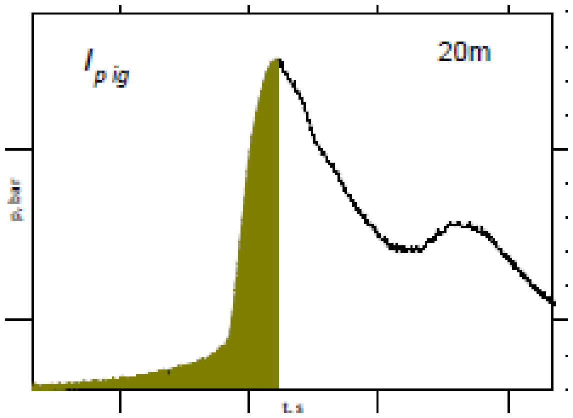
TIC	Rock Dust Type	NIOSH Test #
50%	TRD	4-6-8
50%	NTRD	5-7-9
60%	TRD	1-3-11
60%	NTRD	2-10

Explosion Pressure Time Histories



Explosion Intensity





Nominal TIC	Average Impulse at 100 m ($I_p/I_{p\,ig}$)
60% TRD	7.7 (# 1, 3, 11)
60% NTRD	11.8 (# 2, 10)
50% TRD	15.6 (# 4, 6, 8)
50% NTRD	16.7 (# 5, 7, 9)

Polish Testing Conclusions

- Inerting properties of the treated rock dust (TRD) are at least as good as those of the non-treated rock dust (NTRD)
- Experimental results suggest better performance of the treated rock dust at TIC values larger than 50%

Limitations

Tests conducted using homogenous coal dust/rock dust mixtures

- No layering of dusts

Due to location, shipment of US dusts is cost prohibitive

Tests conducted in higher relative humidity

- (75% – 92%)

Review of Stockton Mine Testing

Measured respirable dust downwind of application

- Treated rock dust
- Untreated rock dust

Moisture infiltrated untreated rock dust before application

Applied the mine's supply of rock dust to cover

Administrative controls necessary when applying rock dust

Experience with Treated Rock Dust

Untreated Rock Dust Application in Mine

Experience with Treated Rock Dust

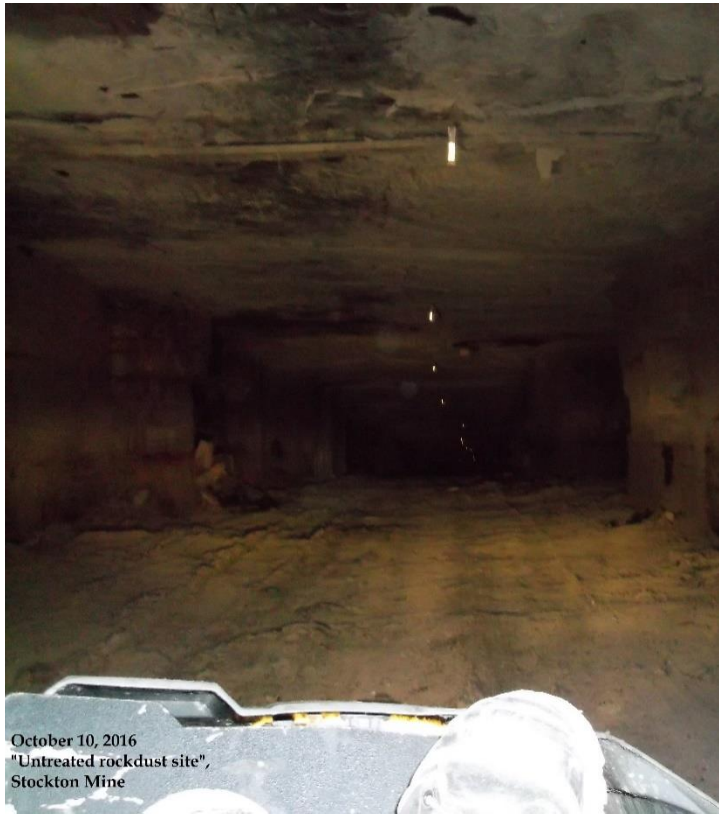
Treated Rock Dust Application in Mine

Experience with Treated Rock Dust

Untreated Rock Dust

Initial Application

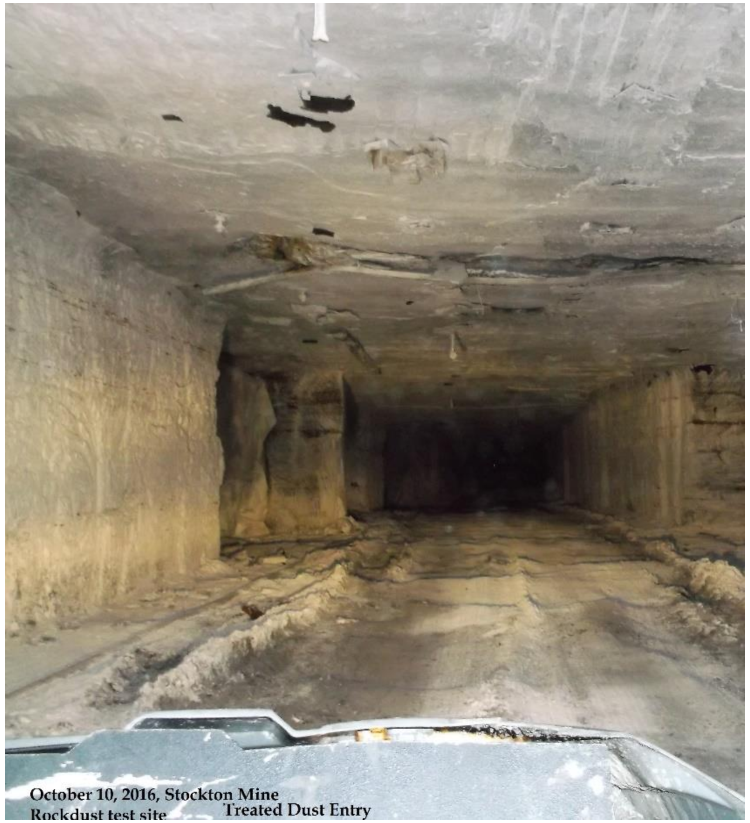
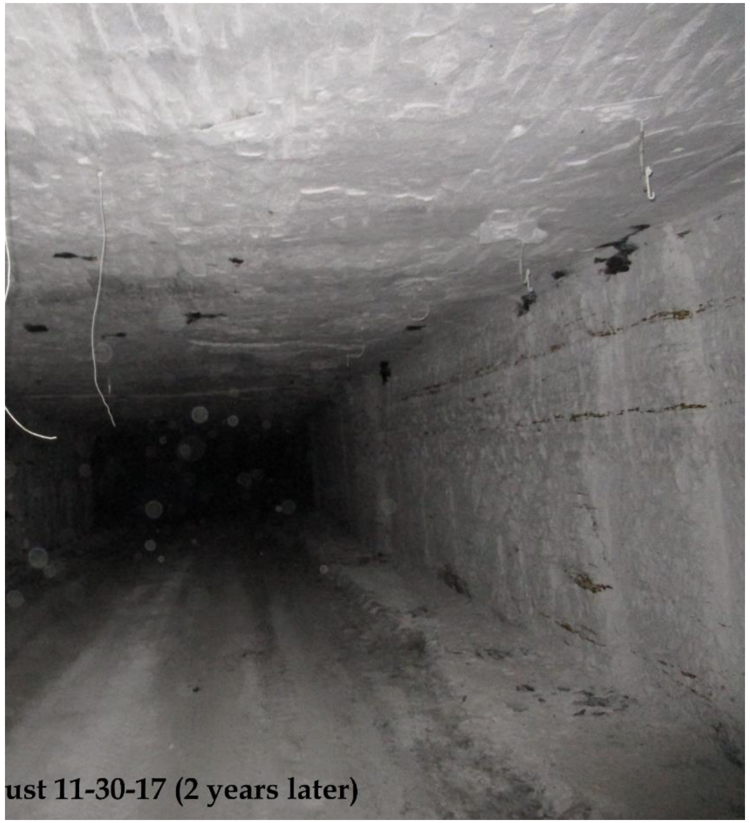
1 Year Later



2 Years Later

Experience with Treated Rock Dust

Treated Rock Dust

Initial Application	1 Year Later	2 Years Later
		

Comments from Others with Experience Using Treated Rock Dust

Engineered Rock Dust

Why Engineered Rock Dust?

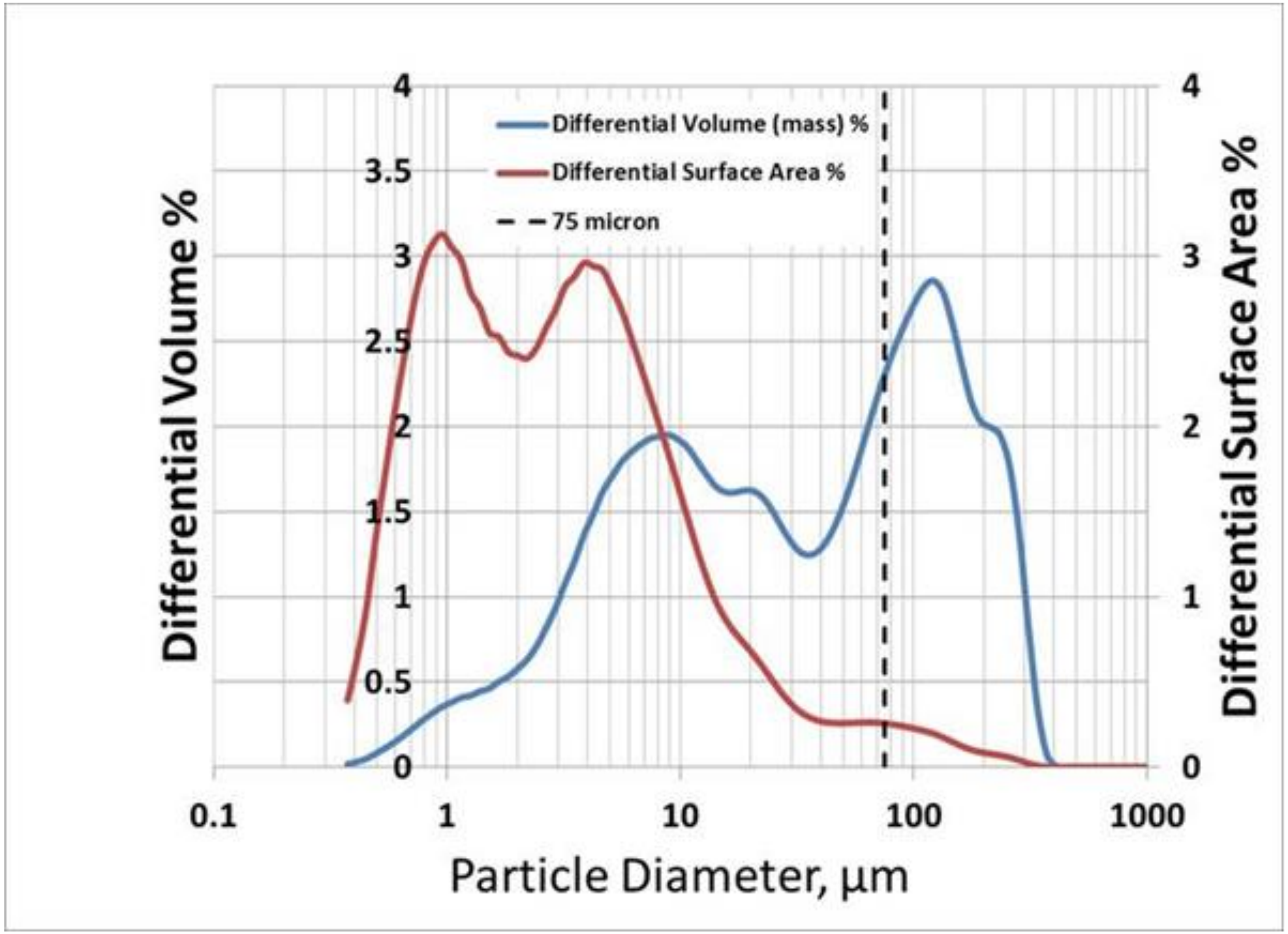
- Reduce or eliminate respirable component of the rock dust
- Hence,
  - Should not contribute to CPDM readings
  - Should not contain respirable silica particles

Ideal Engineered Rock Dust

- It should be as effective as the dry rock dust used to support 80% TIC rule
- Should remain dispersible when applied to wet surfaces

Particle Size Analysis and Distribution

Reference rock dust



- ~30% of the mass
- ~3% of the surface area

Classified RD using

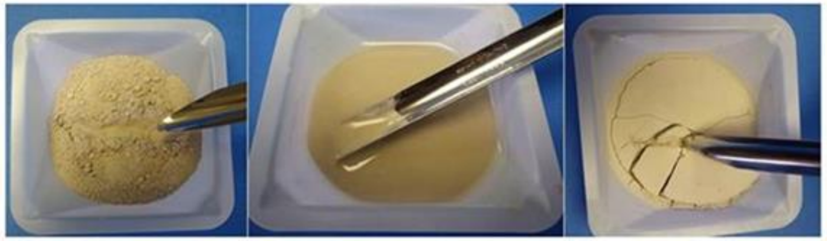
- Ro-Tap
- Air Jet Sieve

Performance Assessment Methods

- Beckman-Coulter Particle Size Analyzer
- 20-L Explosibility Test Chamber [ASTM E1515]
- Dust Dispersion Chamber
- Simple Caking Test

Beckman Coulter Optical Particle Size Analyzer

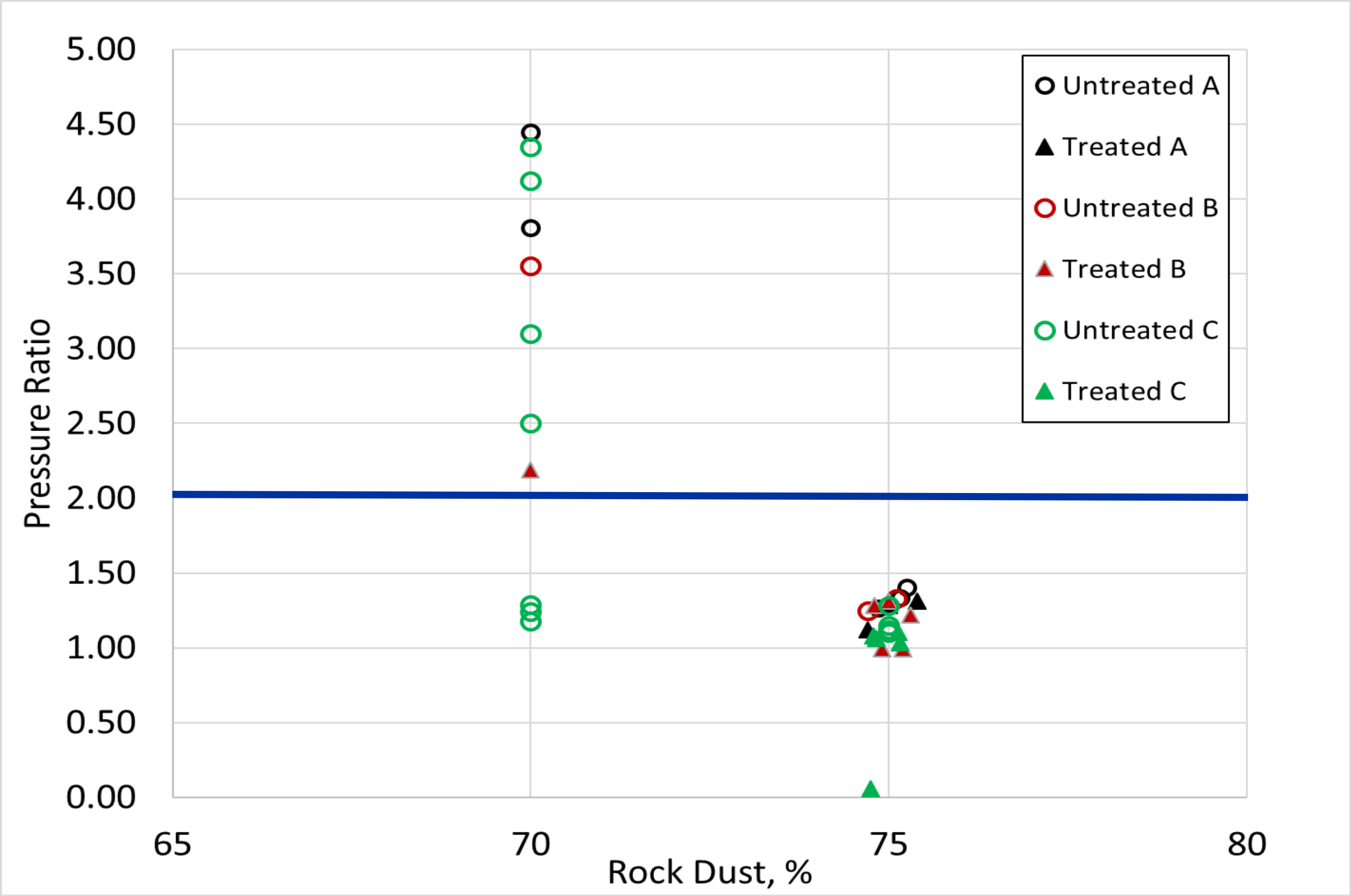
Not wetted | Wetted | Wetted then dried



Simple Caking Test

"Overview of dust explosibility characteristics". Journal of Loss Prevention in the Process Industries [2000], 13, pp.183-199, Cashdollar, K.L.

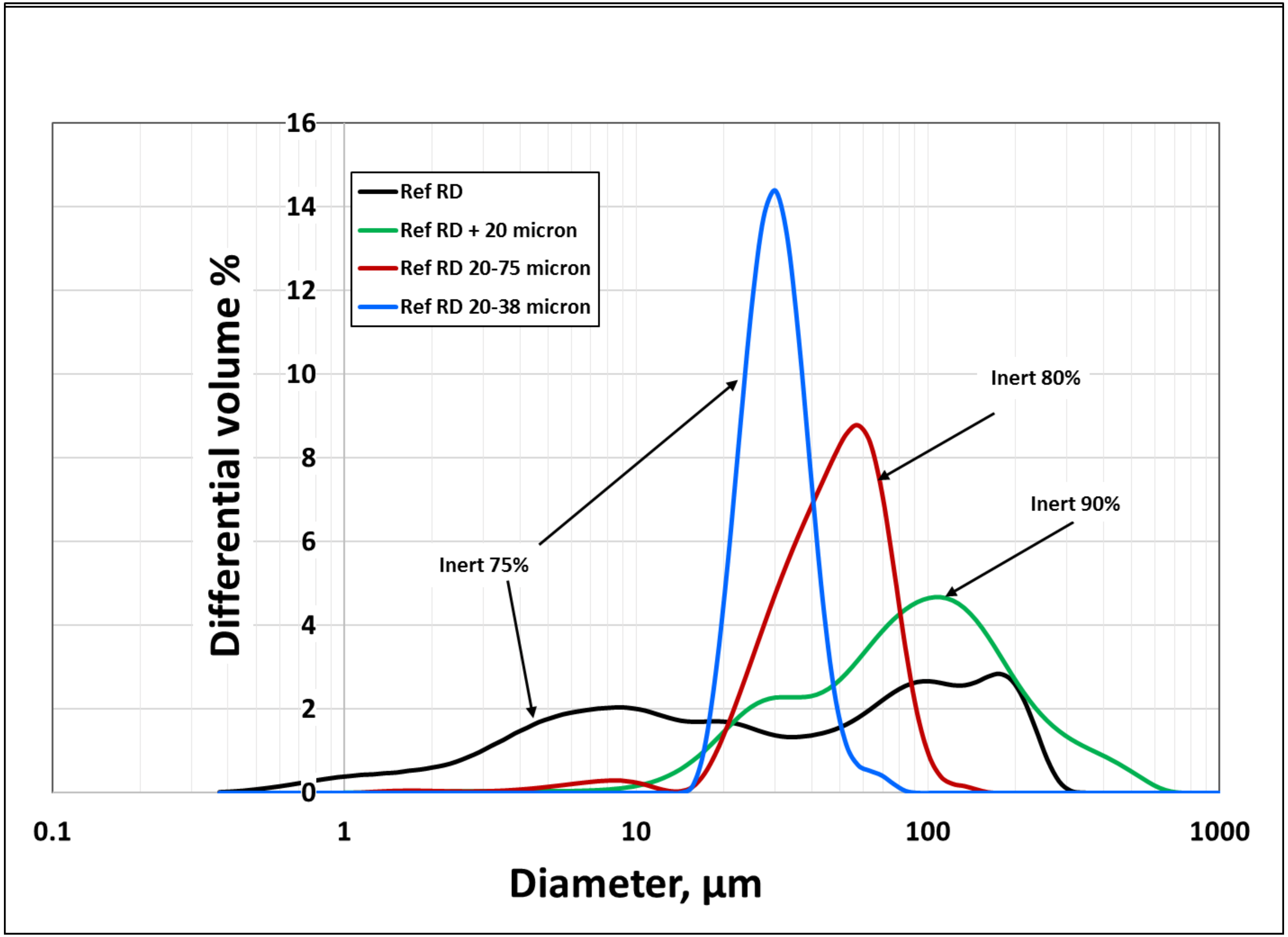
20-L Explosibility Chamber Results for the Rock Dust as received – Treated and Untreated



Criteria for an explosion:

- The maximum explosion pressure ≥ 2 bar
- The volume normalized rate of pressure rise
  $(dP/dt)\ V^{1/3} \geq 1.5$ bar-m-s^{-1}

Inerting Relationship of Engineered Reference Rock Dust

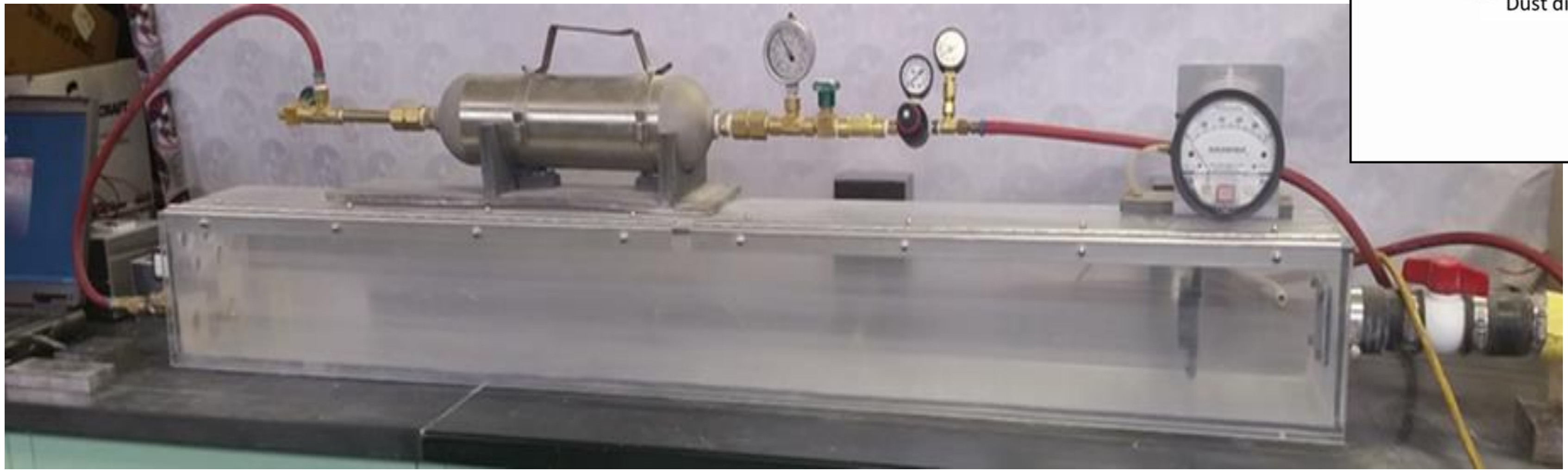


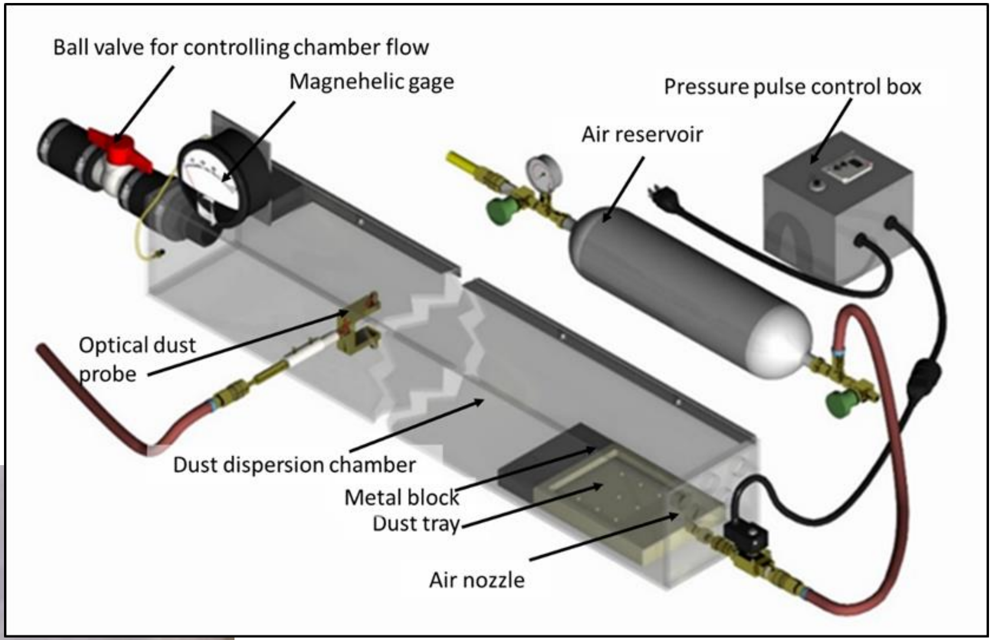
20-L Explosibility Chamber Results for the Engineered Rock Dust

	Treated RD	Untreated RD
Size Fraction, µm	Inert at 75%	Inert at 75%
20-38	**Inert**	**Inert**
20-75	**Explosion**	**Explosion**
38-75	**Explosion**	**Explosion**
minus 38	**Inert**	**Inert**
minus 75	**Inert**	**Inert**
As-received rock dust	**Inert**	**Inert**

Dust Dispersion Chamber

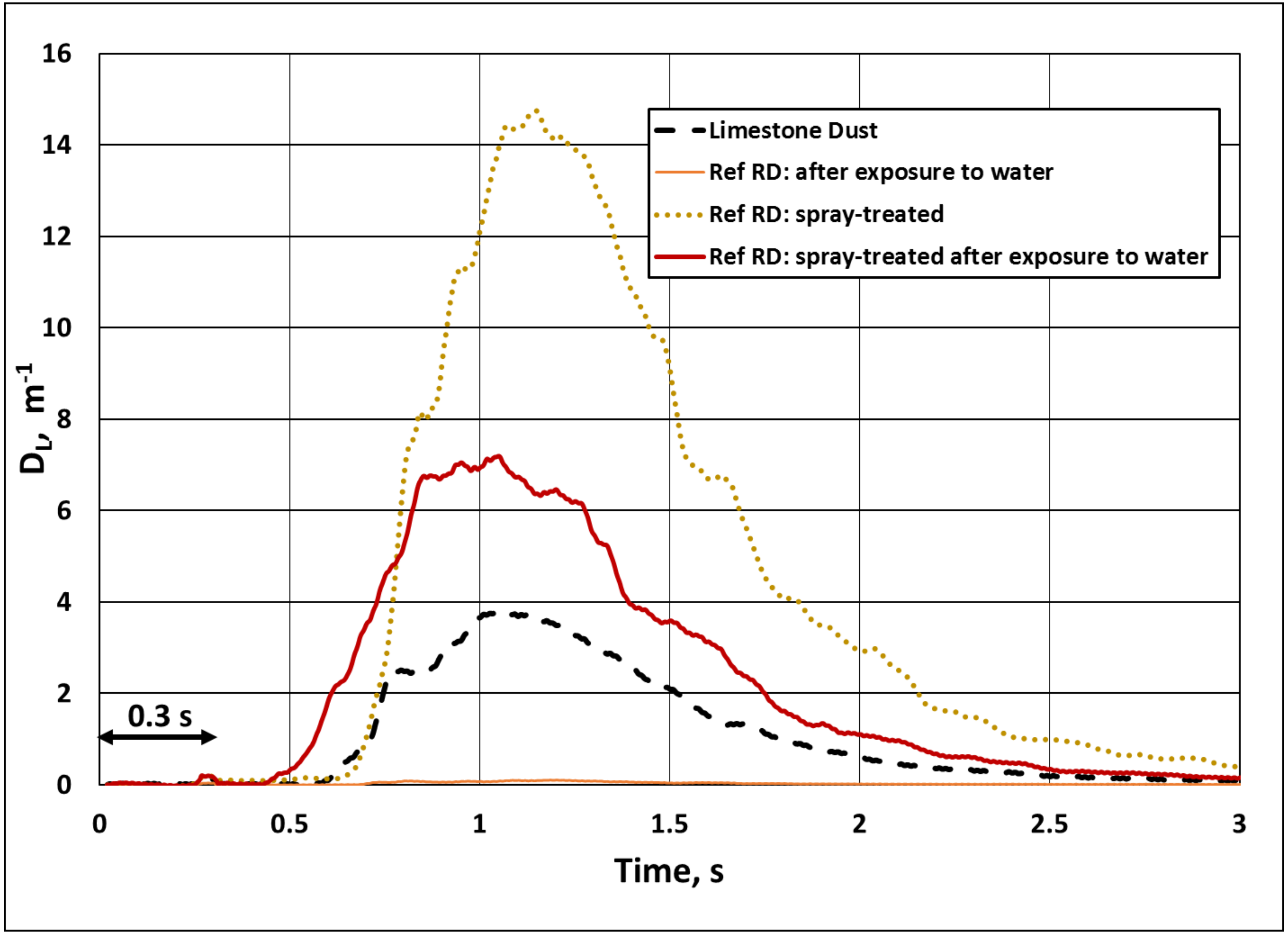
- Based on LLEM coal dust explosion data
- Generates a reproducible air pulse
- 4.2 psi for 0.3 sec





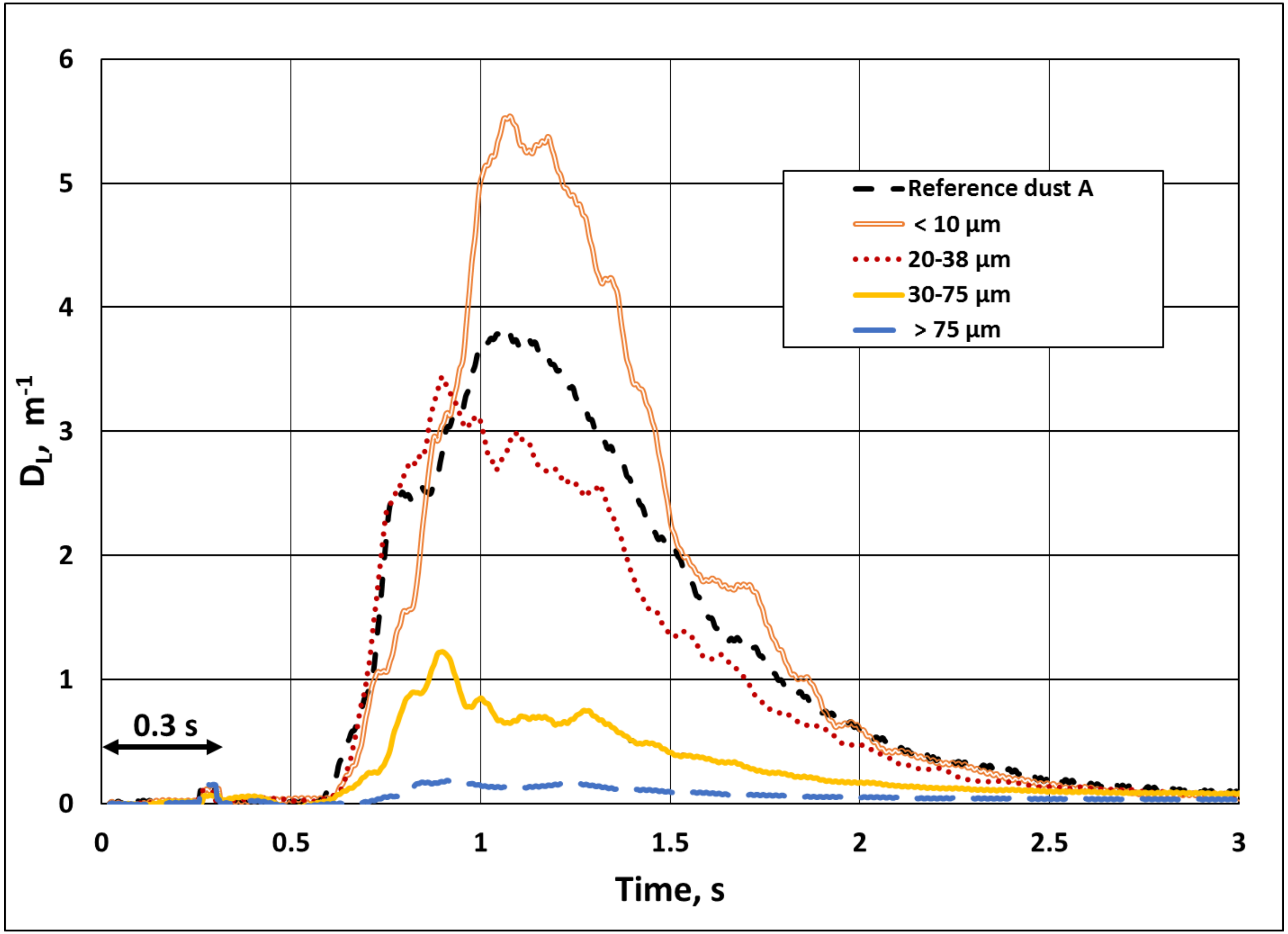
"Design and development of a dust dispersion chamber to quantify the dispersibility of rock dust", Journal of Loss Prevention in the Process Industries [2016] Vol. 39, pp 7-16, Perera et al.

Dispersion of Treated and Untreated Dusts After Moisture Exposure



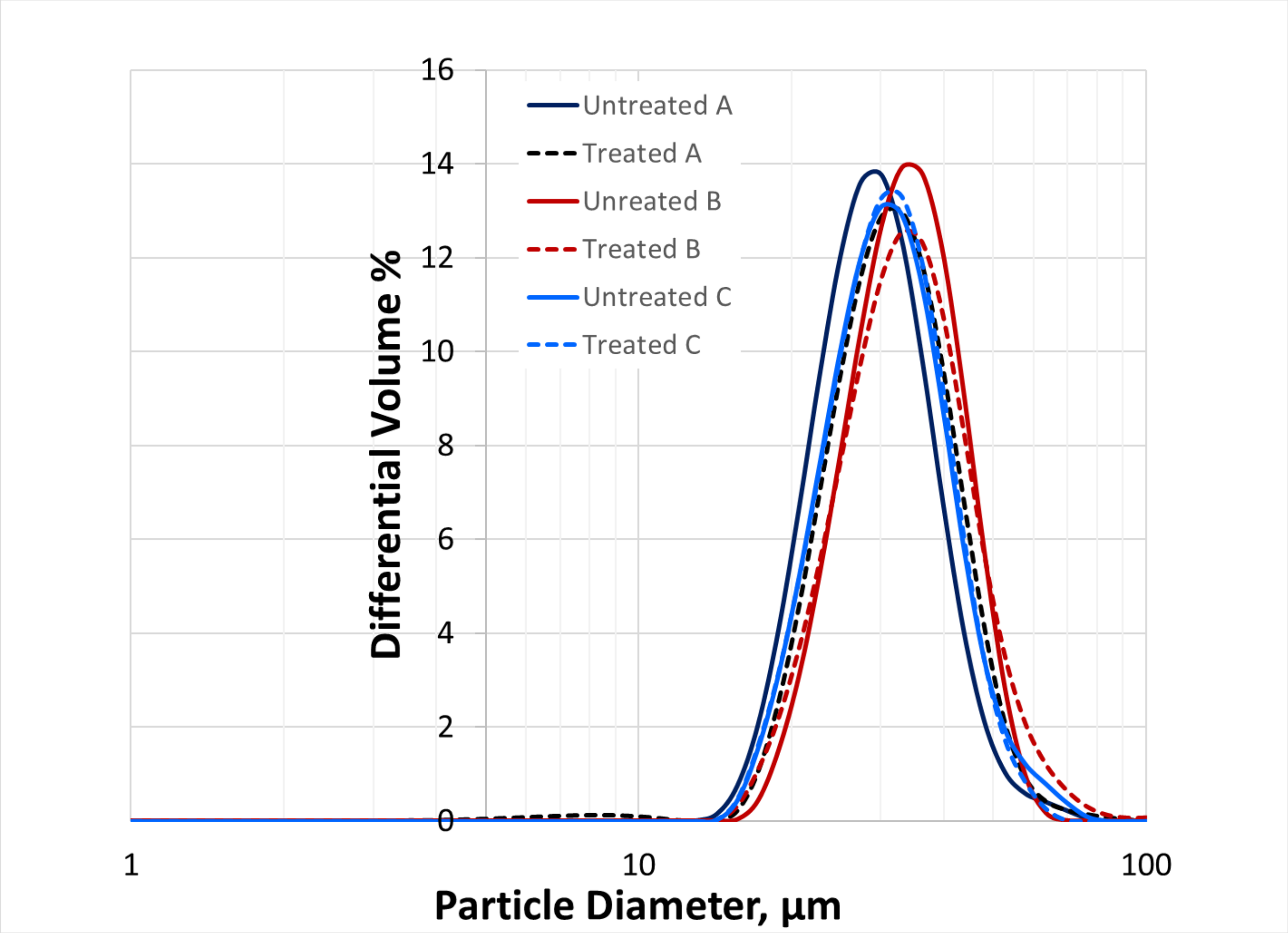
Will the Engineered Rock Dust disperse as well as the Reference dust?

Dispersion of Engineered Reference Rock Dust



Will the Engineered Rock Dust (Treated and Untreated) inert as well as the Reference dust?

Engineered Rock Dust 20-38 μm

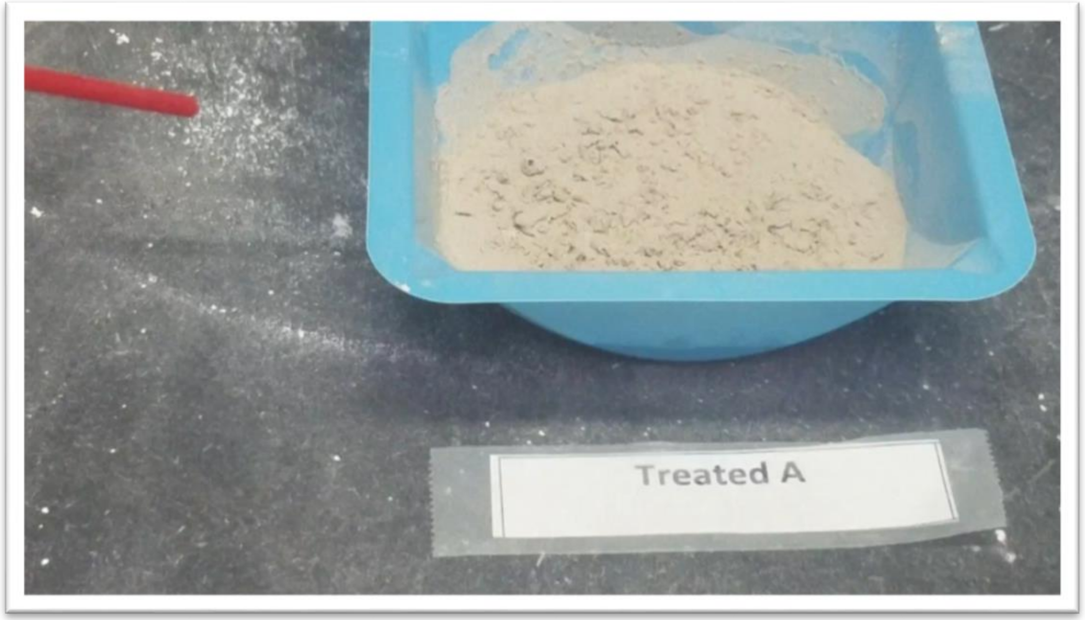


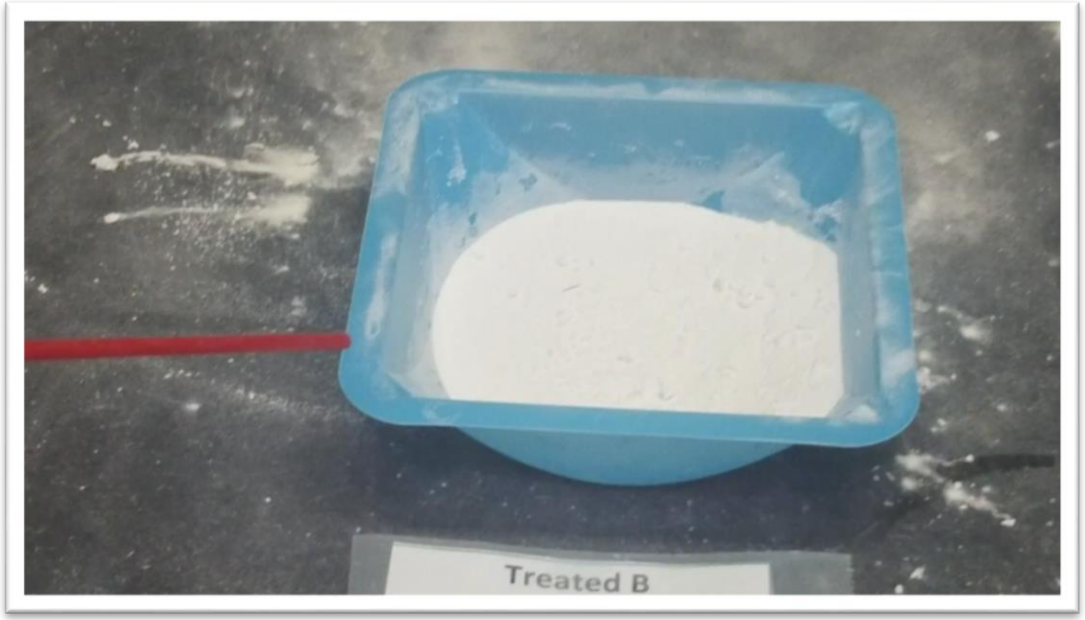
Rock Dust	20-L chamber Results at 75% RD
Untreated A	Inert
Treated A	Inert
Untreated B	Explosion
Treated B	Explosion
Untreated C	Inert
Treated C	Inert

Will the Engineered Rock Dust (Treated) disperse when wetted and dried?

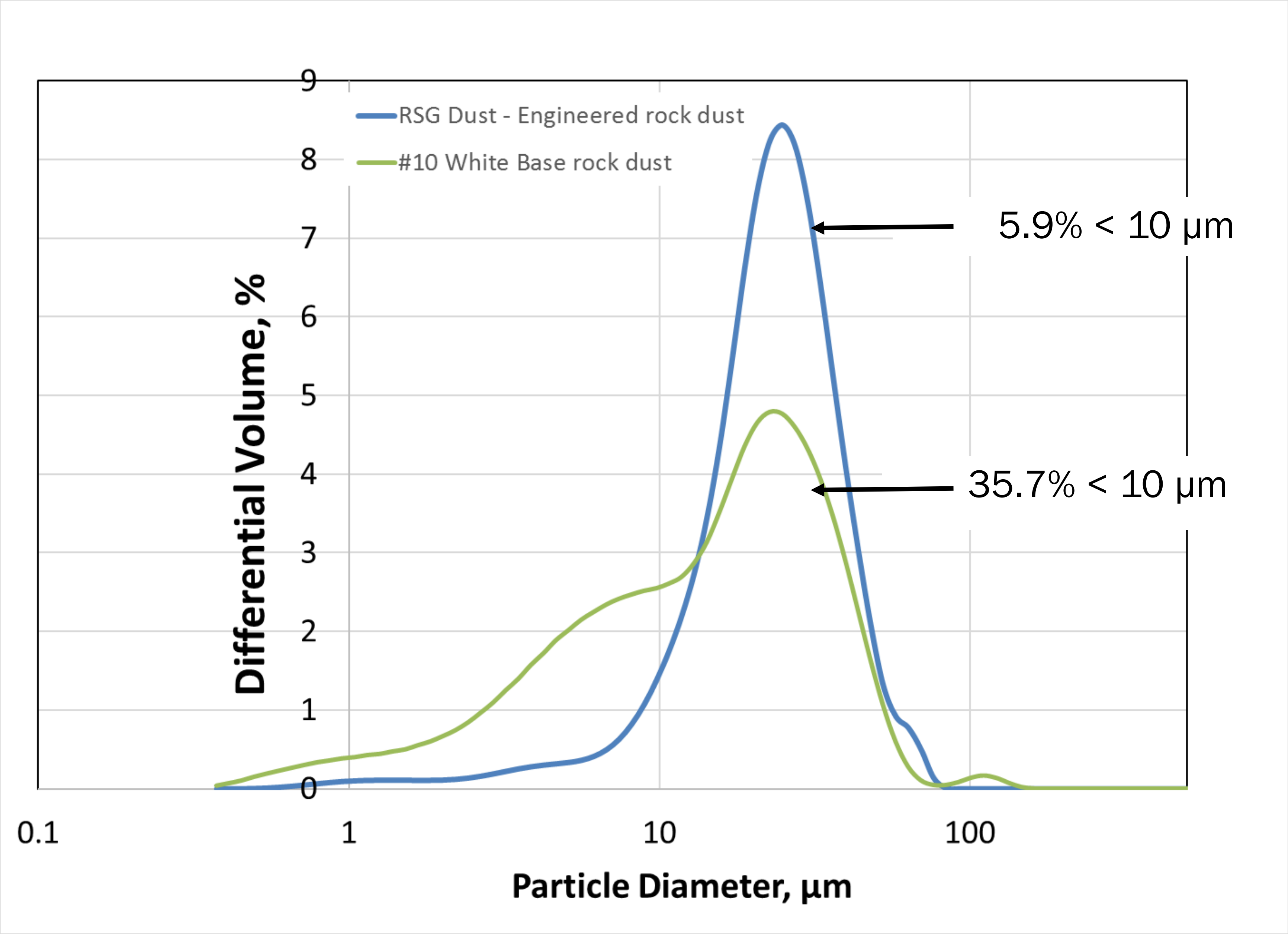
Simple Caking Test with 20-38 micron size fraction of Treated Rock Dust

Simple Caking Test with 20-38 micron size fraction of Treated Rock Dust





Pilot Scale Engineered Rock Dust Particle Size



Preliminary Full-scale Dispersion Results

200 lb of RD dispersed

- Pilot Scale Classified Rock Dust
- Reference Rock Dust

CPDM positioned 100 ft and 500 ft downwind

			Average PDM Dust Concentrations		
	Air Velocity	< 10 µm	Intake	100 ft	500 ft
	ft/min	%	mg/m^3	mg/m^3	mg/m^3
Pilot Scale Classified Rock Dust	95	5.9	0.03	43.24	28.84
Pilot Scale Classified Rock Dust	232	5.9	0.04	20.84	17.33
Reference Rock Dust	221	32.5	NA	131.61	94.80

Ideal Engineered Rock Dust

If we can eliminate only the < 15 micron size fraction instead of < 20 micron, that would provide more surface area

Which means…

- Will have better inerting effectiveness
- Able to maintain 20-L chamber inerting limits
- May lift better with the smaller coal dust particles

Technical success (inerts in the 20-L) but practical failure (cost, time).

Concerns regarding the preferential dispersion of coal dusts.

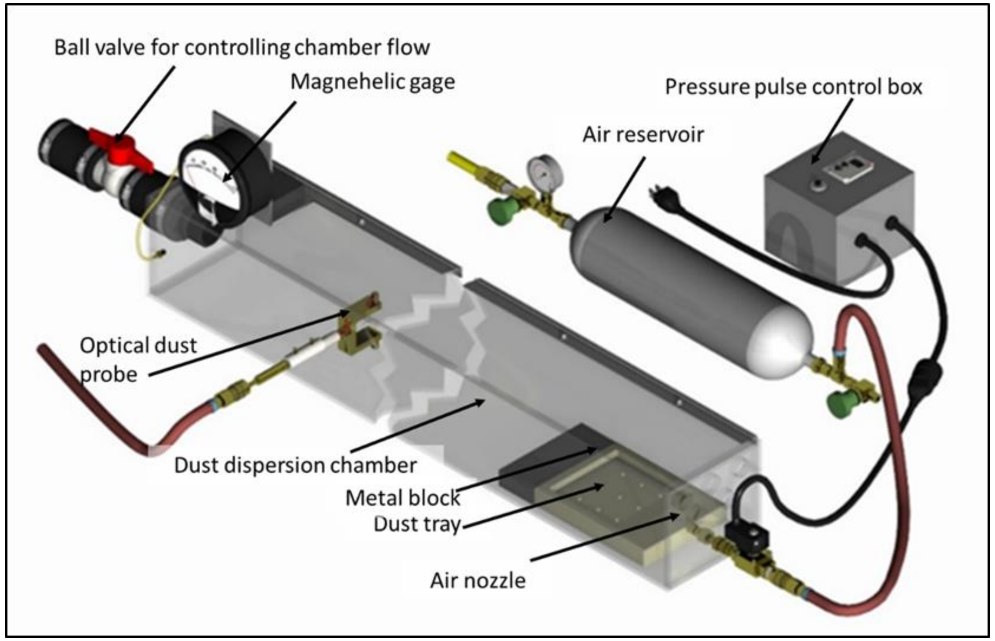
Foamed Rock Dust

Ideal Foamed Applied Rock Dust

- Applied wet
- Adheres to ribs/roof
- Stable in high humidity conditions
- When dry, is as dispersible as the rock dust supporting the 80% TIC rule
- Inerts as well as the rock dust supporting the 80% TIC rule
- Generates very little respirable dust

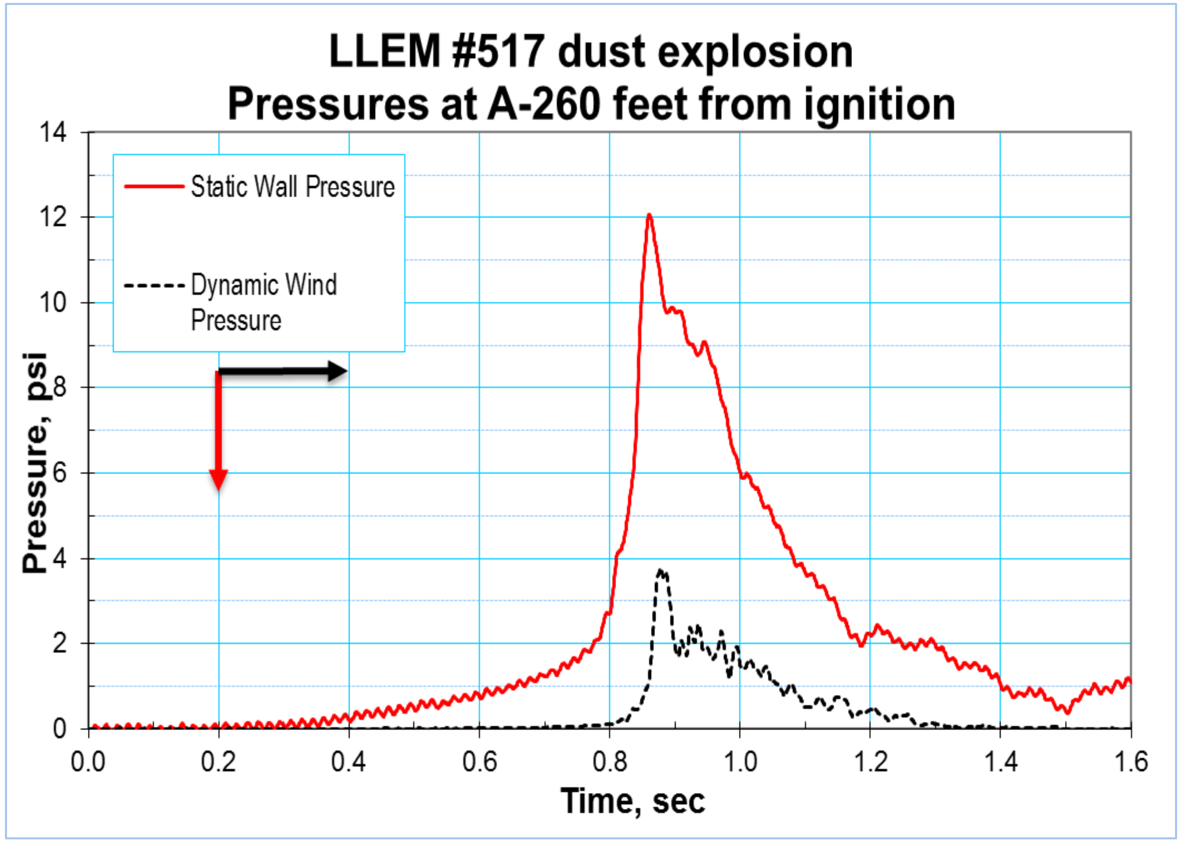
Dust Dispersion Chamber

- Based on LLEM coal dust explosion data
- Generates a reproducible air pulse
- Nozzle orientation is parallel to the tray sample



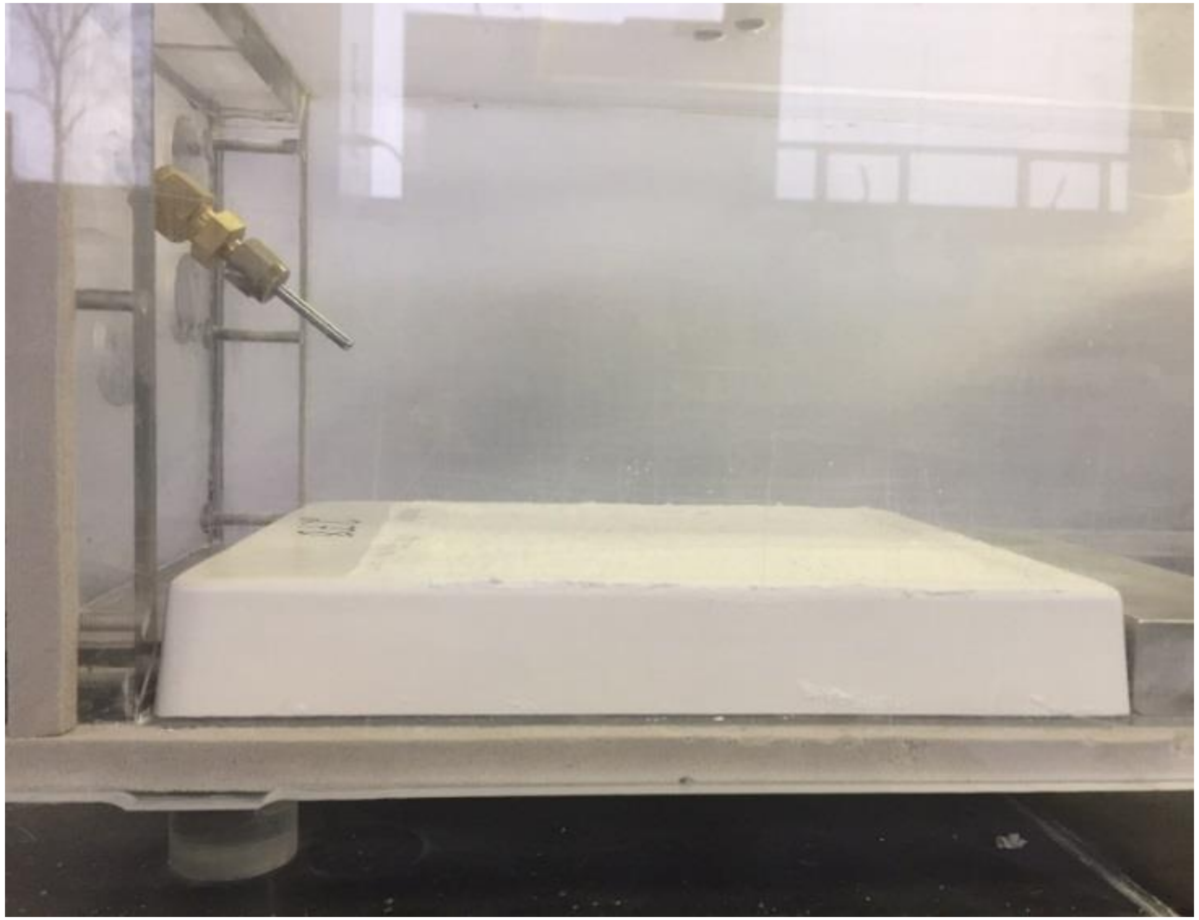
"Design and development of a dust dispersion chamber to quantify the dispersibility of rock dust", Journal of Loss Prevention in the Process Industries [2016] Vol. 39, pp 7-16, Perera et al.

Nozzle orientation of the dispersion chamber limited the perpendicular force otherwise observed during an explosion

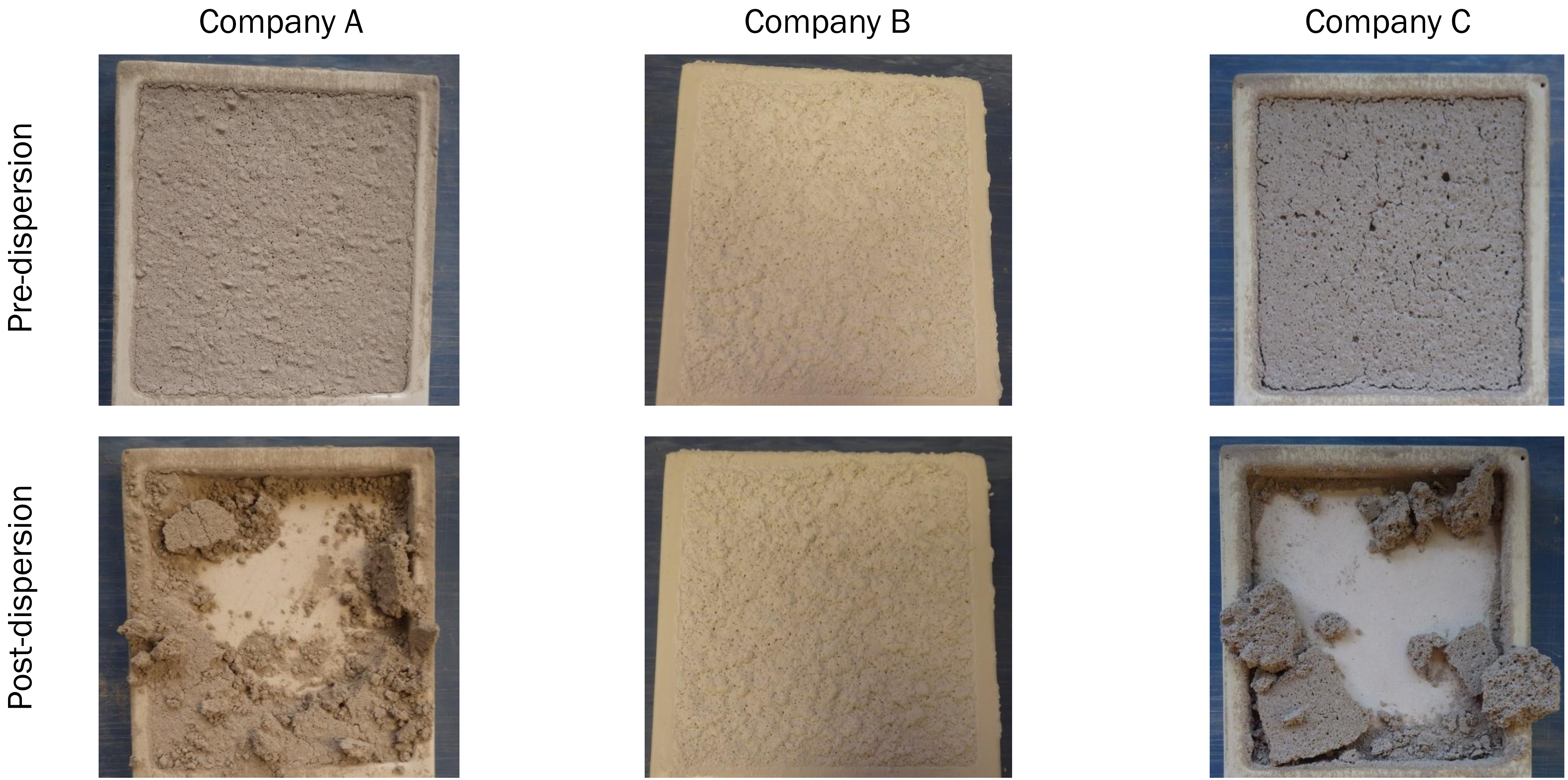


Modifications of the dispersion chamber allow for vertical loading of the samples

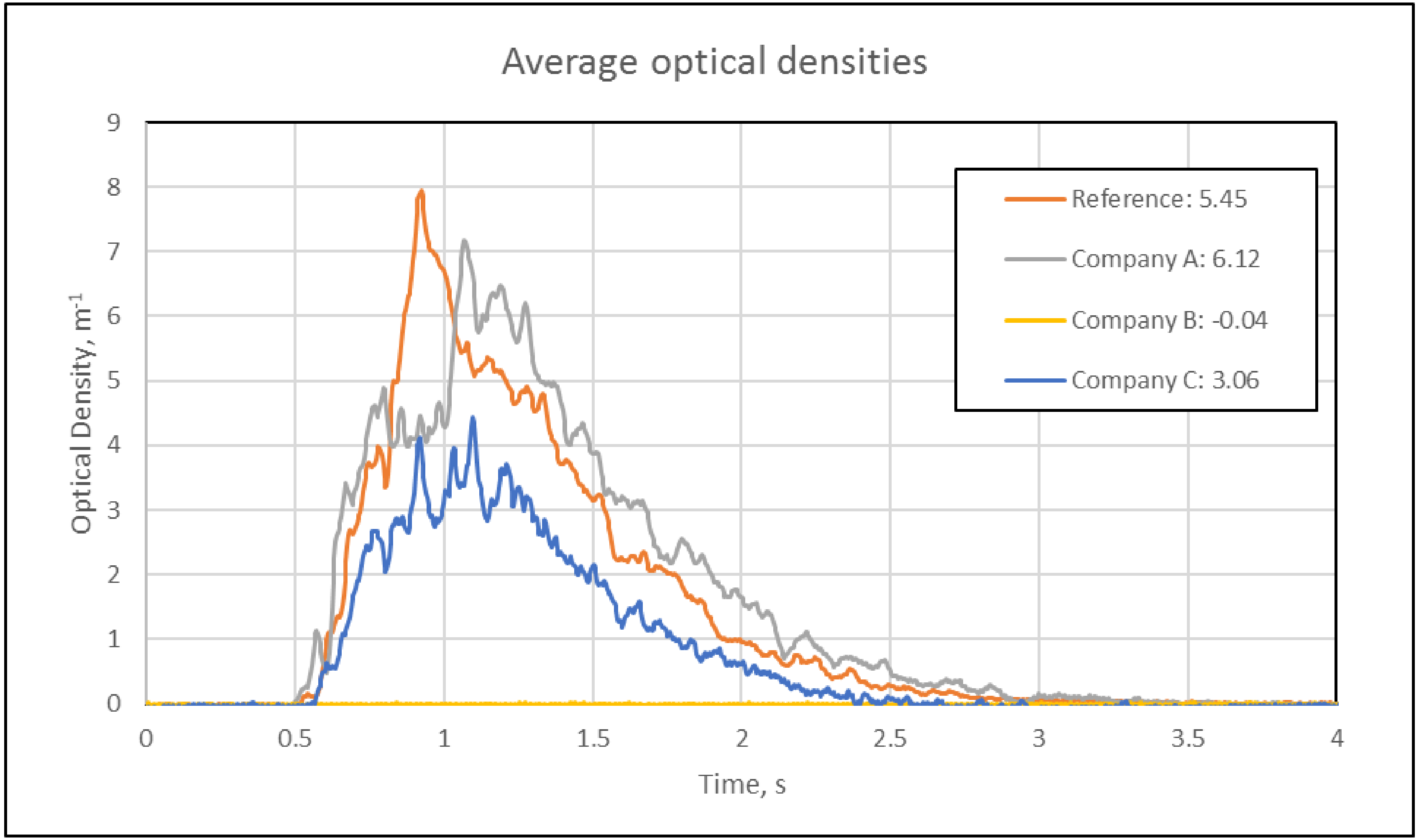
- does not simulate the passing of a shockwave
- induces additional vertical pressure via the rapid release of the air jet.



3 foamed rock dust samples were tested

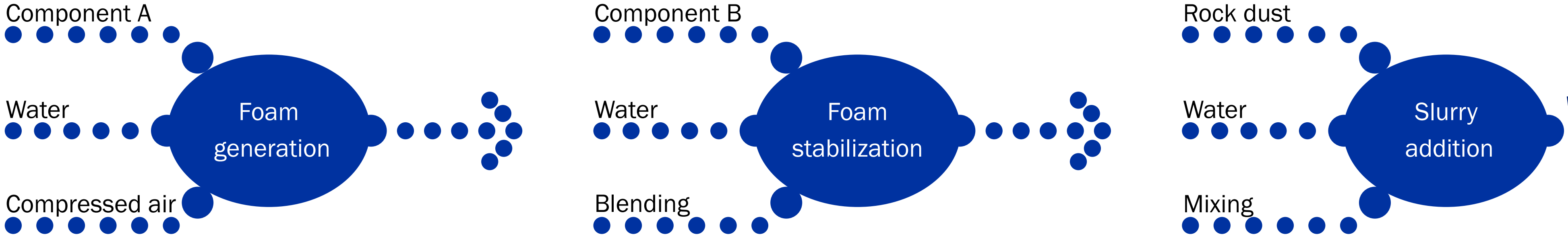


1 sample resulted in the same dispersion characteristics as the reference rock dust



BEM Pilot scale testing of foamed rock dust

Foam preparation Flow chart



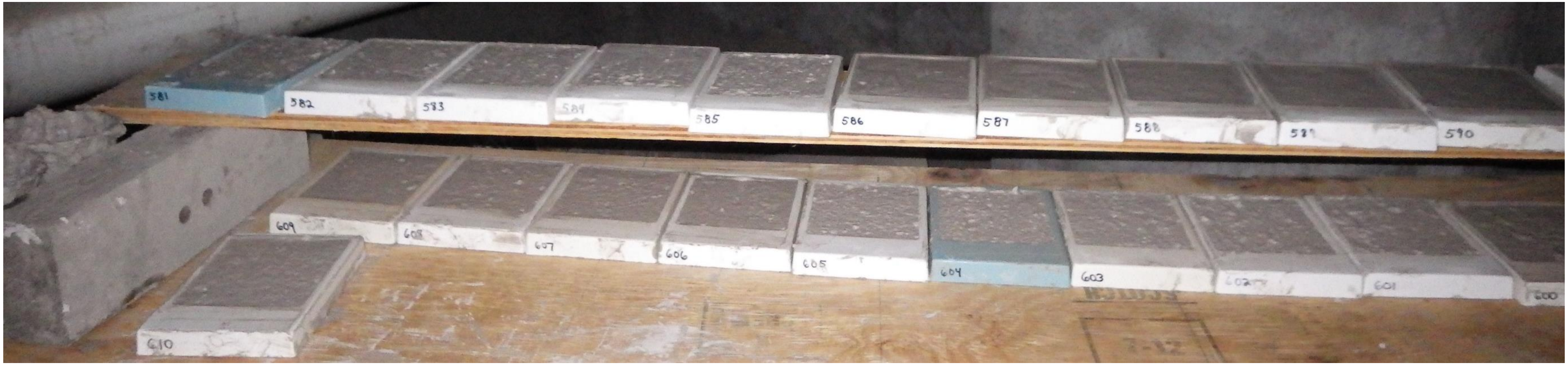
What was done

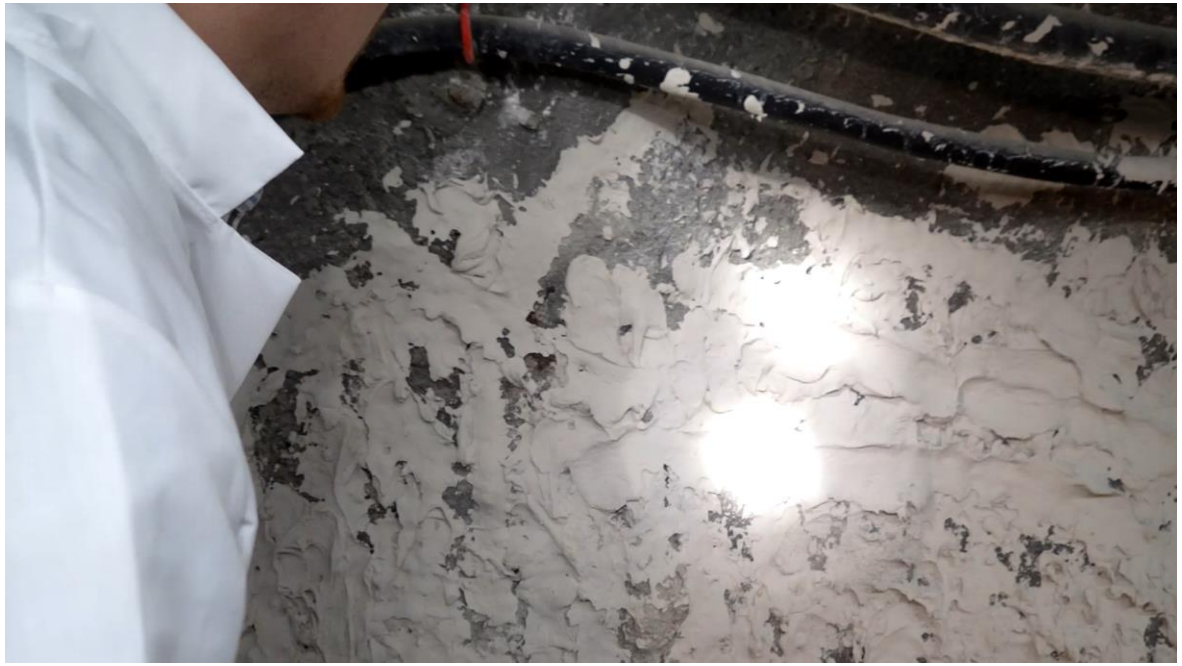
- A total of eleven tests were conducted.
- Two sections were used for shakedown tests.
- Three sections were sprayed with the best performing formulation from lab study and applied with a “shower” nozzle.
- One test section was run with the same formulation without the nozzle attachment
- One test section was run with the same formulation with a “Putzmeister” nozzle
- Two test sections were run with ± 15% rock dust
- Two test sections were run with ± 15% of the additional water used to pre-wet the rock dust

Measurements to be made

Assessment of foam dispersibility via the “canned air” as well as samples collected in trays for testing in the dispersion chamber.

Measurement of foam drying times by periodically recording the weights of foam samples and taking rib samples for moisture analysis.





Foamed Rock Dust

Current formulation shows the most promise in laboratory testing

Additional engineering required to optimize the application process

Need to know how the foam will react to a shockwave

- Large-scale testing

Future partnership assistance to locate underground application site

Moving Forward – Next Steps

Larger-scale testing at Polish CMI

- Layers of coal/rock dust - treated vs untreated
- Foamed rock dust

Engineered rock dust

- Technical success vs practical failure
- Questions regarding preferential dispersion of the coal dust
- No further action planned

Foamed rock dusts

- Pursue continued optimization of the foam mix
- Pursue application optimization
- Request partnership support for underground testing – test site

Toxicity – back burner

Cost/Benefit analyses

Thank You

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