24-008

Alteration and Geochemistry of Clinkers in the San Juan Basin, New Mexico

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ABSTRACT

Clinkers are the result of a seam of coal catching fire and burning the surrounding rocks. The fires caused the surrounding rocks to be baked at high temperatures, removing organic material and partially forming glass. These rocks become hard, orange, and brick like, forming clinker. The purpose of the study is to determine their potential to contain economic levels of critical minerals, including Rare Earth Elements. Some clinkers contain over 200 ppm total REE.

INTRODUCTION

The San Juan Basin consists of 24 individual coal fields present in New Mexico. Coal mining has been conducted in the state since the late 1800s, with the San Juan basin becoming heavily developed during the early and mid-20th century. Extensive mining operations took place for over a century in the Basin with numerous recent large operations taking place and countless small pits being operated. The majority of the coal resources found in the San Juan Basin are late Cretaceous in age, and are part of the Menefee and Crevasse Canyon formations of the Mesa Verde Group, and the Fruitland Formation. [1] The coal resources of the San Juan Basin are extensive, and typically occur in lensed shapes of varying thicknesses [2]. Coal seams that have, through erosion and time, become exposed to the elements can gradually break down into humates over time. Clinkers are found in areas where underground coal fires have taken place, altering the coal seam and the surrounding rock layers. Clinker deposits can be found in the Gallup, Bisti, and Standing Rock coal fields within the San Juan Basin, all areas extensively mined for coal deposits. (Figure 1). These deposits represent sedimentary beds that surrounded coal seams that burned underground for long periods of time, exposing the surrounding layers to extreme heat.

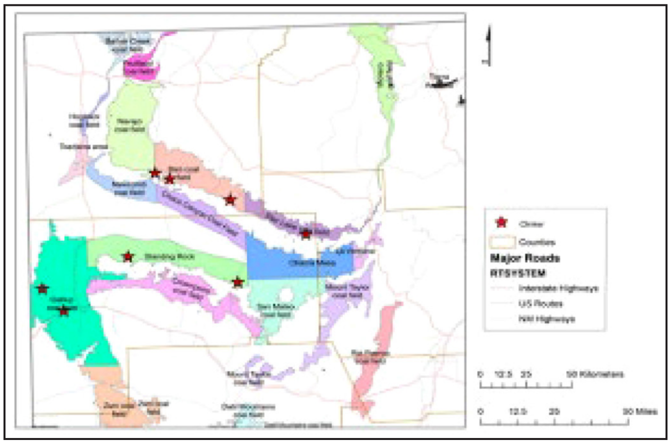

Figure 1. Map showing clinker deposits (stars) and coal fields (colored polygons) in the San Juan Basin of northwestern New Mexico

Clinkers are composed of former sedimentary rocks that laid under and over coal seams, that surrounded coal seams that have been pyro-metamorphized due to exposure to extreme temperatures. The coal seam would catch fire at an exposed surface juncture through various means ranging from spontaneous-combustion as a result of the breakdown of pyrite, to wildfires or lightning strikes igniting the exposed coal. The fire would spread underground, burning up to temperatures of 1000°F [5] and drawing oxygen through fractures in the rock. The intense heat would burn away organic material from the surrounding sedimentary rocks, as well as melting silica and clay minerals to form glasses. Iron minerals in the sedimentary rocks would oxidize, giving the rocks a reddish orange to yellowish appearance (Figure 2). Their also resistant to weathering, and commonly occur as either capstone outcrops that can act as buffers to erosion for underlying coal and resource deposits, or they can present as thick bed deposits that overly and underly burned coal seams (Figure 3).

Currently, clinkers are used industrially as aggregate for road and construction purposes and some specific clinkers are refined down to powders as additives for glass and metal working processes [9].

Critical minerals and REE (Rare Earth Elements) are vital to modern technologies, and are used in electronics computer chips, processors and other vital components. The growing world population and ever advancing technologies require an increased demand of critical minerals resources. Domestic geological features within the United States are currently being looked at as potential sources of domestic production of critical minerals and REE, reducing the need for importation from overseas markets.

Figure 2. Red Dog Fm Clinker rock, El Segundo Mine

Figure 3. Clinker beds transitioning into Coal beds, Left to right, San Juan Basin

We hypothesis that the pyro-metamorphization of the sedimentary rocks could have caused a change in the chemical characteristics of the pyro-metamorphized rocks, potentially making them a source of REE and other critical minerals that can be mined domestically.

METHODS OF STUDY

The methods used to research the hypothesis is the collection of clinker samples from around the San Juan Basin for analysis purposes. Samples were submitted to a laboratory for whole rock and trace element chemistry to provide a clear picture of what elements and minerals are present and in what concentrations to determine the economic viability for the clinkers to contain REE and other critical minerals. Petrography aids in identifying minerals present within the rocks that correlate with the chemical analysis, and provide insight into how the pyro-metamorphization affected the rock and its internal structure. XRD (X-Ray Diffraction) provides insight into what minerals are present in the rock as well as identify minerals that could not be identified in the petrographic analysis. Electron microprobe analysis (EMPA) will be conducted in the future to confirm the chemical analysis in the future.

CHEMISTRY RESULTS

When we compare the coal to the clinker, we can see very similar chemistries. In comparison to chondrite normalization [8], coal (Figure 4) and clinker (Figure 5) are slightly enriched in LREE while being average or slightly depleted in Heavy Rare Earth Elements HREE.

Clinker chemistry has been normalized to Average European Shale and Average Upper Crust for Sedimentary Rock standards to give an idea of how the clinkers compare to other sedimentary deposits. This lets us see whether the clinkers are enriched or depleted compared to other rock types from around the world, giving an idea of their

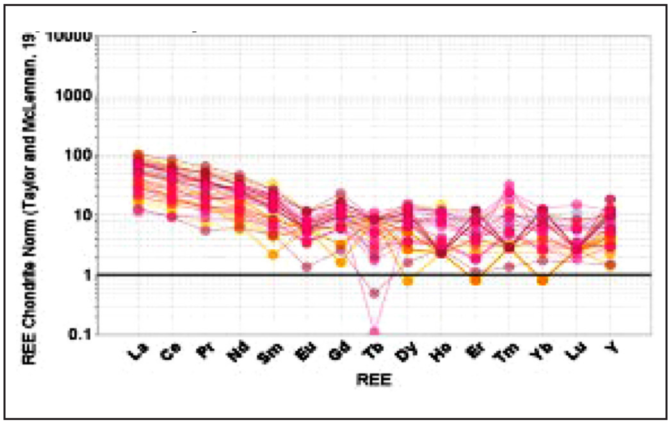

Figure 4. Chondrite normalized patterns of Coal

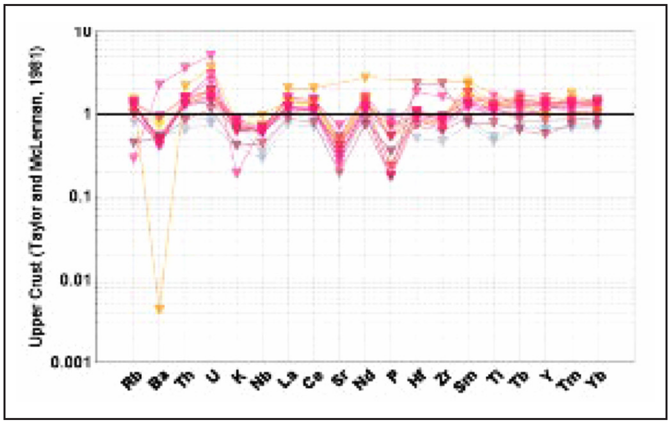

Figure 6. Clinker normalized to Average Upper Crust for Sedimentary Rocks

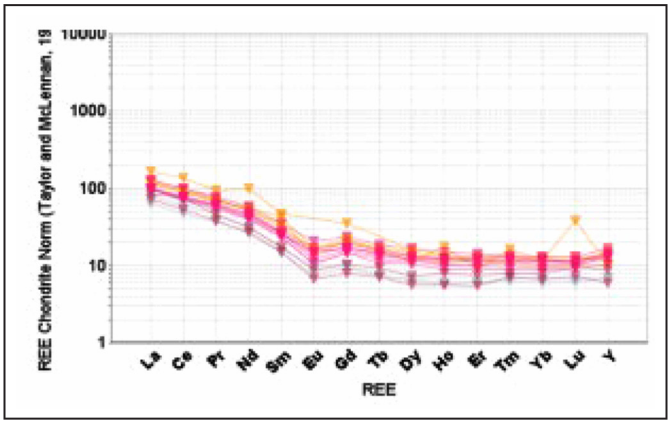

Figure 5. Chondrite normalized patterns of Clinker

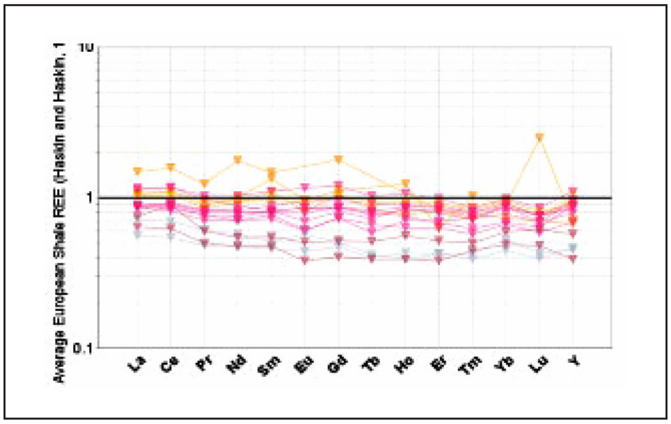

Figure 7. Clinker normalized to Average European Shale

potential for values of critical minerals and REE. If values are enriched in comparison to the average of other sedimentary rocks, which means that clinkers are higher in critical minerals and REE and makes them to be economically potential important resources of critical minerals.

In comparison to Average Upper Crust for Sedimentary Rock values, some of the critical minerals and REE in clinkers are enriched or depleted. Figure 6 shows that uranium (U) is slightly enriched with respect to the standard, while barium (Ba), potassium (K), niobium (Nb), strontium (Sr), and phosphorus (P) are all depleted with respect to the standard.

A similar comparison for REE can be made when the clinker has been compared to the Average European Shale values. Figure 7 shows that some clinkers are slightly enriched in REE while most are depleted in REE when compared to the Average European Shale. In general, heavy REE are more depleted than light REE with respect to standard values. One data point shows erratic REE enrichment and may be a suspect analysis.

The highest total rare earth elements (TREE) value found in any clinker has been relatively low with only 323 ppm TREE, however a positive correlation has been seen between Al_2O_3 and TREE, which suggests that REE may be found in or adsorbed onto clay minerals. Some clinkers are enriched in Al_2O_3, up to 40%.

The highest critical minerals currently found in clinkers have been lithium (Li) (70 ppm), vanadium(V) 114 ppm, nickel(Ni) 108ppm, and zircon(Zr) 557 ppm. Zircon has been shown to have a slightly postive trend in relations to TREE found in clinker, suggesitng REE correlates with Zircon.

PETROGRAPHY AND XRD (X-RAY DIFFRACTION)

Several samples have had petrography performed with transmitted light microscopy. The dominant minerals present in all samples examined have been quartz, clay minerals, and hematite. The amount of each of these minerals varies per sample.

XRD has been conducted on 16 samples of clinker. The minerals presented through the XRD analysis are varied through each sample. Glass is present in all sample in some amount, and varies from sample to sample depending on the conditions the samples were exposed to. The intense heat caused silicas in the rocks to melt, forming glasses, and the amount of glasses present depended on the heat. Silicates that formed in high temperatures, like cristobalite, are present as a result of being altered by the heat [10].

COAL9 is a pyro-metamorphosed mudstone with grains of quartz present as well as small sections of mobilized quartz melted into glasses. (Figure 8). Dull orange-brown in coloration, the sample is rich in hematite that has come from organic sources. Small pieces of rutile are also present, observable as bright red crystals. Metallic gray hematite is also present, not yet oxidized (Figure 9).

COAL28 is a claystone/mudstone clinker containing abundant clay minerals. It also contains pyrobitumen, a baked coal interbedded with the layer when it burned (Figure 10). Rutile is present as fine red crystals with hematite staining visible everywhere, small pockets of quartz are also present but not as prevalent as the clay minerals (Figure 11).

COAL36 is a fine-grained quartz arenite rich in iron oxide (Figure 12). Bedding is defined by variations in grain size and quartz content. Minerals observed are quartz, clay minerals and is hematite rich (Figure 13).

Coal 88 is a modestly sorted sandstone with abundant angular-subangular quartz grains (Figure 14). Clay grains can be seen throughout the matrix that is moderately hematite stained (Figure 15).

Coal 89 is a mature arkose sandstone, with rounded grains suggesting a granitic source (Figure 16). Feldspars and microcline are present, showing distinct twinning of microcline. Biotite is present as small brownish crystals. This sample was not exposed to high temperatures as little glass is present in the sample (Figure 17)

Figure 8. Coal 9 thin section slide polarized light scan

Figure 10. Coal 28 thin section slide polarized light scan

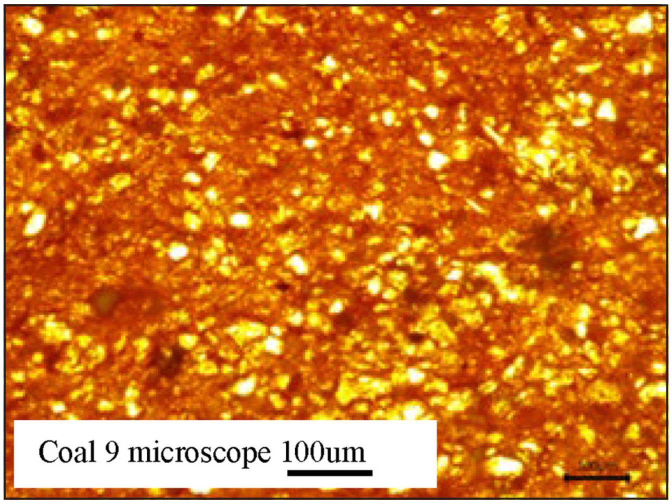

Figure 9. Coal 9 Plane polarized Light microscope image, Mobilized quartz pocket with slight hematite mineralization

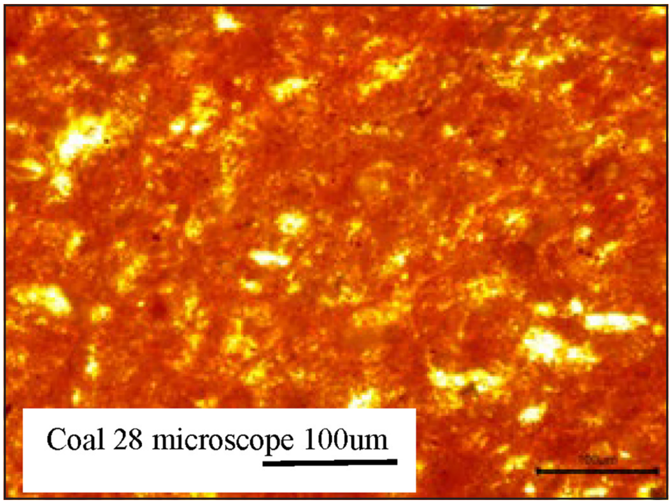

Figure 11. Coal 28 Plane Polarized Light microscope image. Clay mineralization with hematite staining

Figure 12. Coal 36 thin section slide polarized light scan

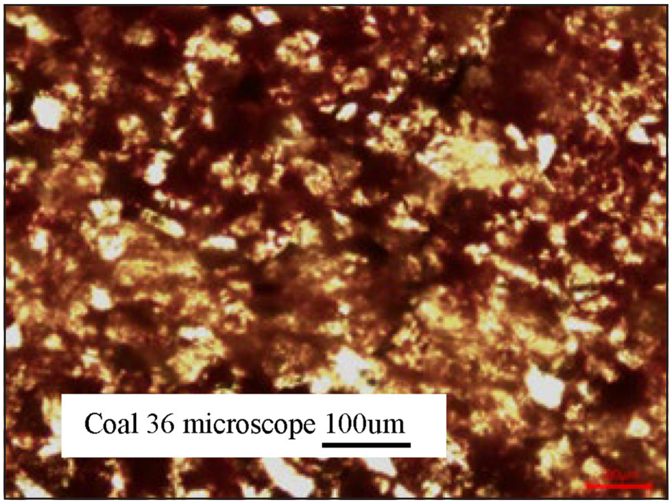

Figure 13. Coal 36 Plane Polarized Light microscope image. Quartz rich bedding layer with dark hematite staining and slight hematite crystallization

Figure 14. Coal 88 thin section polarized light scan

Coal 107 is a clinker composed of interbedded shale, siltstone, and sandstone (Figure 18). Note the differences in grain size, shape, and color (Figure 19). This sample is

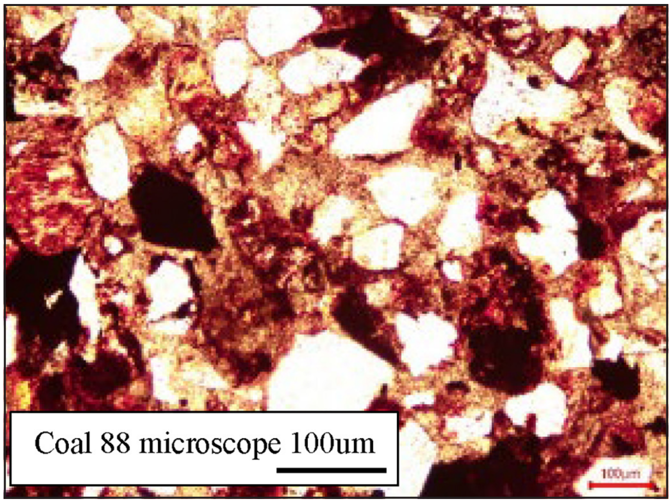

Figure 15. Coal 88 Plane Polarized Light microscope image. Evident angular quartz in modestly sorted sandstone, kaolinite and hematite staining present in abundance

Figure 16. Coal 89 thin section polarized light scan

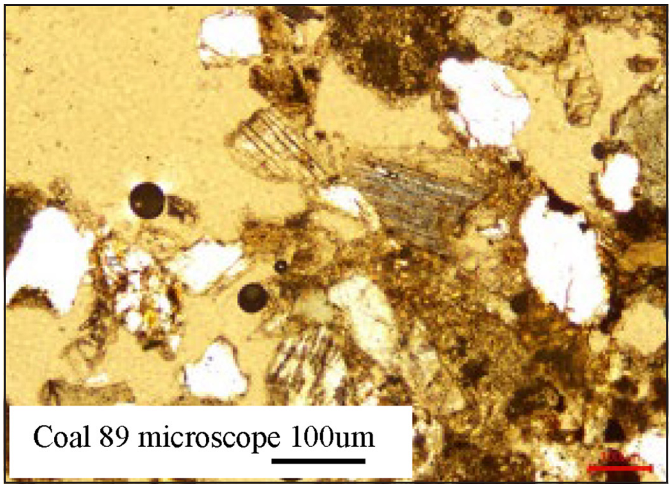

Figure 17. Coal 89 reflected Polarized Light microscope image. microcline grains are present in a feldspar and quartz rich matrix

Figure 18. Coal 107 thin section polarized light scan

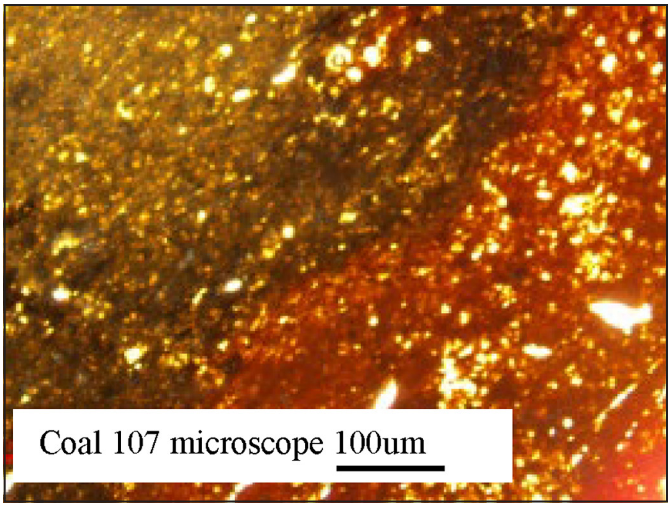

Figure 19. Coal 107 Plane Polarized Light microscope image. The different interbedded layers are distinctive by the differences in color, grain size, and grain shape.

hematite rich and was exposed to high temperatures with a high glass content.

Coal 108 is a highly altered sedimentary rock that was exposed to very high temperatures with a melted/fused nature (Figure 20) mullite and cristobalite, both high temperature silicate minerals, are present as a possible result of pyro metamorphization from the high temperatures this sample was exposed to (Figure 21, Figure 22).

Coal 140 is a high temperature clinker that has a low iron oxide percentage. It shows high glass content and fusing of the minerals (Figure 23). Feldspars are present through the sample with a high amphibole concentration, possibly cummingtonite (Figure 24, Figure 25). Material for this sample is a potassium rich protolith from the minerals seen in the sample.

Figure 20. Coal 108 thin section polarized light scan.

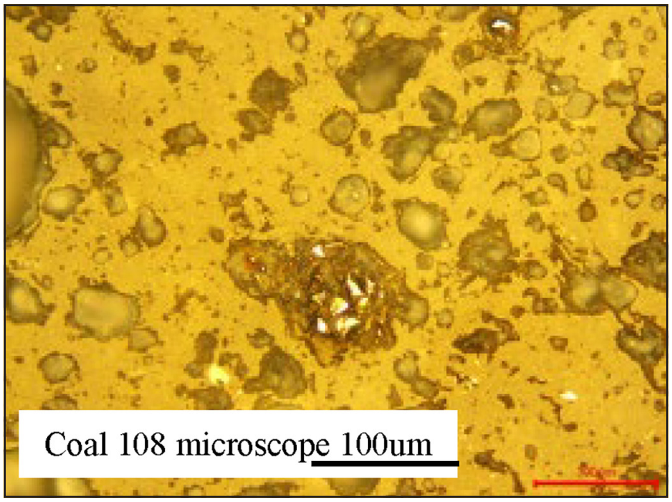

Figure 21. Coal 108 reflected light. Mullite crystal in the matrix

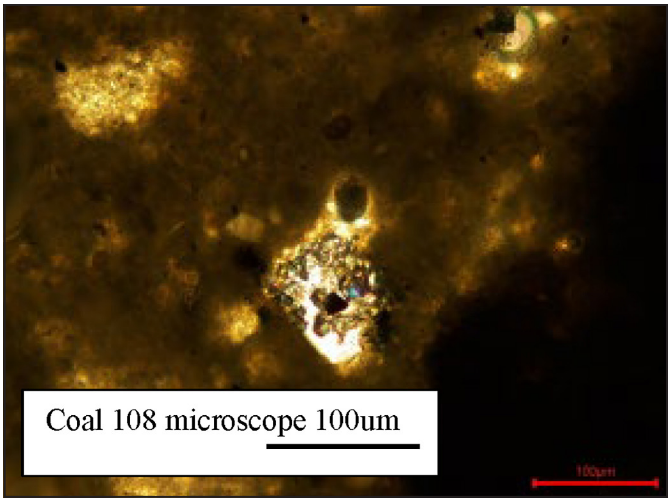

Figure 22. Coal 108 reflected cross polarized light. Mullite crystal in matrix

Figure 23. Coal 140 thin section polarized light scan

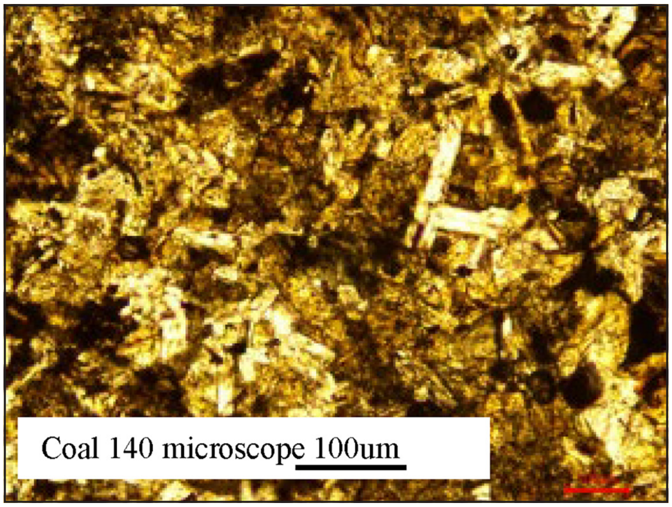

Figure 24. Coal 140 plane polarized light

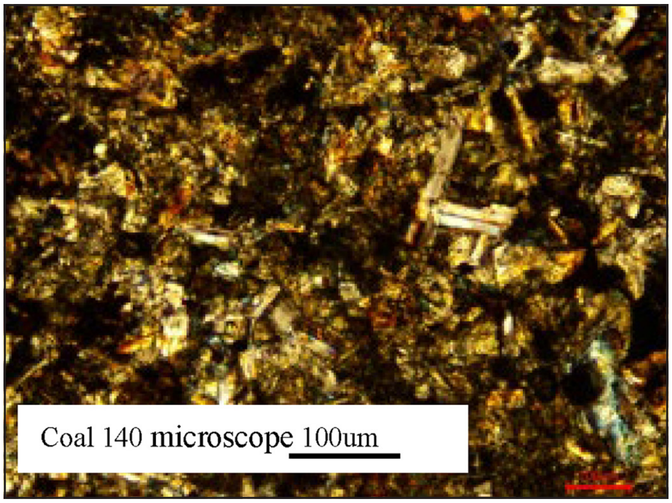

Figure 25. Coal 140 cross polarized light. High birefringence of the amphiboles is evident

MINERALOGY

Table 1 is a summary of the minerals present as identified by XRD and petrographic analysis

Table 1. Minerals identified in clinkers through petrography and XRD

Sample Name	Mineral
Coal9	Quartz (SiO_2), Hematite (Fe_2O_3), Rutile (TiO_2)
Coal 28	Quartz (SiO_2), Goethite (a-FeO(OH)), Rutile (TiO_2)
Coal 36	Quartz (SiO_2), Hematite (Fe_2O_3), Kaolinite ($Al_2Si_2O_5(OH)$)
Coal 88	Quartz (SiO_2), Hematite (Fe_2O_3), Calcite ($MgCa(CO_3)_2$), Kaolinite ($Al_2Si_2O_5(OH)$, Unidentified iron mineral
Coal89	Quartz (SiO_2), Albite ($NaAlSi_3O_8$)
Coal 102	Quartz (SiO_2), Hematite (Fe_2O_3)
Coal 104	Quartz (SiO_2)
Coal 106	Quartz (SiO_2)
Coal 107	Quartz (SiO_2), Hematite (Fe_2O_3), Opal (SiO_2 -H_2O), Iron Oxide (Fe_3O_4)
Coal 108	Quartz (SiO_2), Cristobalite (SiO_2), Mullite ($_3Al_2O_3SiO_2$), Cordierite ($Mg_2Al_4Si_5O_{18}$), high glass content
Coal 110	Quartz (SiO_2), Hematite (Fe_2O_3)
Coal 117	Quartz (SiO_2), Kaolinite ($Al_2Si_2O_5(OH)$
Coal 138	Quartz (SiO_2)
Coal 140	Orthoclase ($KAlSi_3O_8$), Albite ($NaAlSi_3O_8$)
Coal 146	Quartz, (SiO_2), Illite ($(K,H_3O)(Al,Mg,Fe)_2(Si,Al)_4O_{10})(OH)_2,(H_2O)$
Coal 167	Quartz (SiO_2)

PRELIMINARY CONCLUSIONS

The data suggests that the pyro-metamorphization of the sedimentary rocks near burned coal seams have not caused any noticeable change in the chemical composition of the clinker rocks. The clinkers do not show economic levels of either REE or other critical minerals, with only low to moderate concentrations currently detected. The relation of TREE correlating with Al_2O_3 suggests REE may be hosted by clay minerals or very fine grained REE minerals.

Clinker does have potential to be a possible resource for Al_2O_3 due to the enriched levels of aluminum oxides.

ACKNOWLEDGEMENTS

This report is part of ongoing studies of mineral resources in New Mexico, supported by the New Mexico Bureau of Geology and Mineral Resources (NMBGMR), Nelia

Dunbar, Director and State Geologist. Current research is funded through a DOE grant Carbon ore, rare earth, and CM (CORE-CM) assessment of San Juan River-Raton Coal Basin, New Mexico, DE-FE0032051. Thanks to the graduate student of Virginia McLemore who helped in sample collection and fieldwork, Special thanks in particular to Zorheh Kazemi Motlagh, Jakob Newcomer, Kyle Stafford, and Megan Badonie, in the collection of field samples and assistance in analytical work. Special thanks is given to Virginia T. McLemore for the opportunity to work on this research and for the support she has given throughout. Any persons wishing to conduct geologic investigations on the Navajo Nation must first apply for and receive a permit from the Minerals Department, P.O. Box 1910, Window Rock, Arizona 6515 and telephone no. 928-871-6588.

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24-009

An Integrated Method to Classify Ground-Fall Accidents and to Estimate Ground-Fall Trends in U.S. Mines Using Machine Learning Algorithms

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ABSTRACT

Ground falls in U.S. underground coal mines can lead to significant consequences, including loss of life, injuries, damaged equipment, and production stoppage. Improving the safety of the workplace is of utmost importance for mine workers and the U.S. economy. The Mine Safety and Health Administration (MSHA) accident/injury/illness dataset provides short narratives for reported incidents, including ground-falls. The main objective of this study is to develop a framework that includes: 1) utilizing machine learning algorithms to categorize ground-fall incidents from narratives based on the main cause of the occurrence and 2) demonstrating an example of a user-friendly visualization to display injury/fatality trends from narratives in U.S. coal mines between 1983 and 2021. The developed framework was tested on a subset of the data and achieved an average F1-score of 96% in categorizing the incidents. The outcome will help identify areas requiring additional research and innovative solutions to reduce severe occupational hazards.

INTRODUCTION

Accidents due to ground-fall failures in coal mines can potentially have severe consequences, including both fatal and non-fatal injuries, damage of equipment, impaired ventilation, and production delay/stoppage. Improving the safety of the workplace in U.S. coal mines is of utmost importance for mine workers, mine operators, and the U.S. economy. Between 2010 and 2019, the ground-fall incidents in U.S. mines resulted in 46 fatalities, 33 permanent disabilities, 3,082 injuries, 119,520 non-fatal days lost, and 12,433 days of restricted work activities (Rashed et al. 2022). In MSHA dataset, the accident/injury/illness datafile combines five different types of ground fall accidents (roof fall, rib fall, face fall, rock outburst, and highwall failure) into two categories called “fall of roof, back, or brow from in-place” and “fall of face, rib, pillar, side, or highwall.” The MSHA dataset provides short narratives for ground-fall incidents; however, it does not classify them based on the root cause of the incident. MSHA fatality reports include the root cause of incidents. However, they are not considered in this study. From a prevention perspective, ascertaining root causes of incidents, often provided in the narratives, is necessary for the research to address mitigation strategies and identifying potential gaps in scientific research. Note that accidents and incidents are used interchangeably in this study.

Rashed et al. 2022 manually classified thousands of ground-fall narratives into five categories using a subset of the MSHA dataset. However, this process was time-consuming and tedious, which is why in this study the authors raised a question about the capability of utilizing machine